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Dynamic Theory of Die Swell for Entangled Polymeric Liquids in Tube Extrusions: New Set of Equations for the Growth and Ultimate Extrudate Swelling Ratios under the Free States

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A new dynamic theory of die swell for entangled polymeric liquids in a steady simple shear flow is proposed which can be used to predict the correlation of the time-dependent and time-independent extrudate swelling behaviors to the molecular parameters of polymers and the operational variables. The theory is based on the O-W-F constitutive equation and the free recovery from Poiseuille flow with different ratios. Experiments show that the magnitudes of the simple shear in the steady simple shear flow may be resolved into the free recoil resulting from the recoverable elastic strains and the viscous heating resulting from the unrecoverable viscoelastic strains. For distinguishing the recoil from the viscous heating, a partition function and two exponential fractions of conformation for the recoil and the viscous heating were defined. Thus the instantaneous, delayed and ultimate recoverable strain, and recoil in the free recovery were correlated to the partition function, the fraction of recoverable conformation, the molecular parameters, and the operational variables. Also the dynamics of the growth equation on the delayed viscoelastic strain and the delayed recoil in free state were deduced. After introducing the condition of uniform two dimensional extensions, the definition of swell ratio and the operational variables into the above correlation expressions and growth equations, then the correlations of the delayed extrudate swelling effect and the ultimate extrudate swelling effects to the molecular parameters and the operational variables were derived. Finally, two new sets of equations on the growth variables and ultimate extrudate swelling ratios under the dynamic and equilibrium states were also deduced from this dynamic theory of die swell. The first set of equations on the ultimate extrudate swelling ratio under the free and equilibrium states was verified by HDPE experimental data at two temperatures and different operational variables. The second set of equations on the growth extrudate swelling ratios under free and dynamic states was verified by PBD experimental data with different molecular weights and different operational variables. An excellent agreement is obtained, which shows that the two sets of equations for the growth and ultimate extrudate swelling ratios can be used directly to predict the correlation of extrudate swelling ratios to the molecular parameters and the operational variables.

Key words: Die swell, Entanglement, Viscoelastic recoil

I. INTRODUCTION

Die swell is an important topic in non-Newtonian fluid mechanics and polymer rheology. To make quantitatively reliable predictions of the extrudate swelling behavior based on bulk flow properties has been a formidable challenge. The extrudate swell behavior is not only determined by the bulk flow properties but also depends on the relaxation dynamics and the residence time during which the fluid travels from the die entry to the exit. The residence time t_f is related to shear rate $\dot{\gamma}$ and the capillary die aspect ratio of length L to diameter D . For Newtonian fluids the relaxation is instantaneous and there is no bulk elasticity on an experimentally accessible time scale, so the extrudate

swell can only be an exit effect. For a polymeric fluid with a predominant relaxation time τ , the elongational stretching due to converging entry flow increases the level of the extrudate swelling ratio B when $\tau > t_f$. This is analogous to the Bagley effect on the capillary flow; this entry flow contribution to the extrudate swell ratio depends on the bulk fluid viscoelasticity. There are several studies on the theory of the elastic recoil and the extrudate swell for viscoelastic fluids in the literature [1-6]. The most pertinent for the extrudate swell of the molten polymers would seem to be that of Tanner [4] which is based on the KBKZ constitutive equation and the unconstrained recovery from Poiseuille flow with $L/D \rightarrow \infty$. It found that B may be expressed as

$$B = \frac{D_f}{D} = 0.13 + \left[1 + \frac{1}{8} \left(\frac{N_1}{\tau_{12}} \right)_w^2 \right]^{1/6} \quad (1)$$

where N_1 and τ_{12} are the first normal difference and the shear stress respectively. This expression gives some in-

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sight into the intrinsic nature of the extrudate swell behavior of viscoelastic fluids. But the viscous heating of viscoelastic fluids in the extrusion and the time-dependent nature of the extrudate swelling behavior of viscoelastic fluids are all not considered. Clearly, an essential requirement to relate the primary structure of the polymer chain with extrudate swell under practical process conditions and to understand the true viscoelastic nature of extrudate swell as a function of time are the availabilities of systemic experimental data and a fundamentally theoretical framework. Recently experimental studies on the correlation of the true viscoelastic behavior of extrudate swell to the primary structure of polymeric chain (\overline{M}_n , $\overline{M}_n/\overline{M}_w$, and \overline{M}_e) and the operational processes condition ($\dot{\gamma}$, τ_{12} , and L/D) have been carried out, respectively, by Koopmans [7] and Wang [8], but the theoretical research on theoretical framework for the correlation has been never reported.

It is well known that at die entrance the polymeric melts are forced to pass through a larger barrel section into a smaller die. It is subjected to a large extension associated with a large entrance pressure drop. The extension and flow can also induce the dynamic and reversible disentanglement and reentanglement between polymeric chains, so that at the die exit the resulting polymeric melts then undergo a partial stress relaxation and produce an extrudate swell ratio. The extension of the stress relaxation and the degree of disentanglement and reentanglement of polymeric chains not only depend on the length-to-diameter ratio and the residence time ($t - t'$) of polymeric chain, but also they directly relate to the change in the conformation of segment and chain and the degree of reorganization of the constituent chains in extrudates. There are three kinds of polymer segments and chains in the extrudates which are defined as extending chain, coil chain and entangled polymeric chain. They are loaded with different forced states (normal and shear stress) and different magnitudes of stress. After removal of the stress the extending segments and chains can produce an instantaneous recoverable elastic strain. The resulting disentangled polymeric chains can also undergo the reformation of entanglement that leads to the delayed recoverable viselastic strain with low speed. Therefore, the study of die swell should concentrate on the change in the conformation of segment and polymeric chain and the degree of disentanglement and reentanglement between the polymeric chains in the transient network of polymer fluids. In our previous works [9-12], we have established a molecular theory of non-linear viscoelasticity for the polymeric melts [9], derived their constitutive equations and material functions in the multiple-flow field at the steady state [10,11], and provided a quantitative verification for the molecular theory [12].

In previous papers [13,14], a new molecular theory of die swell was proposed, which is based on the O-W-F constitutive equation and the free recovery by the mechanism [15] of reentanglement-disentanglement

transition (RE-DT) and recoil-uncoil transition (RC-UCT) from Poiseuille flow with the different L/D . A new set of equations on the ultimate extrudate swelling ratio under the equilibrium state and the correlation of ultimate extrudate swelling effect to the molecular parameters and the operational variables was also deduced from the molecular theory.

In this work, a dynamic theory of die swell was proposed and a new set of equations on the growth and ultimate extrudate swelling ratios under the free and dynamic state was also deduced.

II. A SET OF ULTIMATE EQUATIONS ON THE EXTRUDATE SWELLING RATIO UNDER THE FREE AND EQUILIBRIUM STATE

A. Total free energy of deformations and flow, constitutive equations and material functions of entangled polymeric liquids

1. Total viscoelastic free energy of deformation and flow for the entangled polymeric liquids

The total viscoelastic free energy ΔF_{TT} may be expressed as the sum of the viscoelastic free energy of deformation ΔF_{ET} resulting from the change in conformational free energy of entangled network, and the unrecoverable internal free energy E_{VT} resulting from the change in the internal energy of flow system caused by the molecular interaction between the segments within each constitutive chain. They have been deduced from the model of transient entanglement network, the mechanisms of multiple repetition and the conformational statistical distribution function of entangled polymeric chains by the method of statistical mechanics and kinetics [9,13]. It was found that ΔF_{TT} and ΔF_{ET} may be expressed as [9,13]

$$\Delta F_{TT} = \Delta F_{ET} + E_{VT} \quad (2)$$

$$\Delta F_{ET} = N_T C (t - t')^{n'-1} \exp \left[-\frac{(1 + \tau_d)(t - t')}{\tau_t} \right] \cdot (C_{100} I_1 + C_{020} I_2 + C_{200} I_3) \quad (3)$$

where τ_t , $\tau_d = D_e^\alpha$ are, respectively, the relaxation time of the terminal and loop constituent chains, $t - t'$ is the flow time of fluids in the extrusion, and I_1 , I_2 , I_3 , C_{100} , C_{020} , and C_{200} are defined as follows [9,13]

$$I_1 = \alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 \quad (4)$$

$$I_2 = \ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3} \quad (5)$$

$$I_3 = (\alpha_x^2 + \alpha_y^2 + \alpha_z^2)^2 - 9 \quad (6)$$

$$C_{100} = 0.5KT\xi B_{100} \quad (7)$$

$$C_{020} = 0.5KT\xi B_{020} \quad (8)$$

$$C_{200} = 0.5KT\xi B_{200} \quad (9)$$

where α_x , α_y , α_z are the components of extension ratio α along x , y , and z respectively, K is the Boltzmann

constant, T is absolute temperature, ξ is the number of elastically active chains on each entangled polymeric chain, C_{100} , C_{020} , C_{200} are, respectively, defined as the storage and loss modulus contributing from the different extending elastic segments and from the slipping segments and polymeric chains, the expressions of structural parameters of B_{100} , B_{020} , B_{200} , have been given in reference [9]. N_T is the total number of entangled polymeric chains per unit volume and $C = 1/\Gamma(n')$ is a constant.

2. Constitutive equations and material functions of the entangled polymeric liquids

The constitutive equation and the material function of the entangled polymeric liquids in the simple shear flow at the steady shear rate $\dot{\gamma}$ have been deduced in previous papers [10,11]. It was found that when the memory function $m(t-t')$ is defined as [10]

$$\begin{aligned} \frac{\partial G(t-t')}{\partial t'} = m(t-t') = CG_N^0 & \left[(1-n') \right. \\ & \left. + \frac{1}{\tau_t}(1+\tau_d)(t-t') \right] \cdot (t-t')^{n'-2} \\ & \cdot \exp \left[-\frac{1}{\tau_t}(1+\tau_d)(t-t') \right] \end{aligned} \quad (10)$$

The following expressions are obtained:

(i) First normal-stress difference N_1 in the steady shear flow

$$\begin{aligned} N_1 = \tau_{11} - \tau_{22} = \psi_1(\dot{\gamma})\dot{\gamma}^2 \\ = \frac{2n'\eta_0^{1+1/n'}}{(G_N^0)^{1/n'} [1 + (\eta_0\dot{\gamma}/G_N^0)^\alpha]^{n'+1}} \dot{\gamma}^2 \end{aligned} \quad (11)$$

(ii) Shear stress τ_{12} in the steady shear flow

$$\tau_{12} = \eta(\dot{\gamma})\dot{\gamma} = \frac{\eta_0}{[1 + (\eta_0\dot{\gamma}/G_N^0)^\alpha]^{n'}} \dot{\gamma} \quad (12)$$

(iii) The ratio of N_1 to τ_{12} for the free recoil and viscous heating in steady shear recovery

$$\begin{aligned} \frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}} &= \frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}} = (\tan \Phi)_{S.F}^{\dot{\gamma}} \\ &= \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_{S.F} = n' \left(\frac{\eta_0}{G_N^0} \right)^{1/n'} \\ &\cdot \dot{\gamma} \left[1 + \left(\frac{\eta_0\dot{\gamma}}{G_N^0} \right)^\alpha \right]^{-1} \end{aligned} \quad (13)$$

(iv) First normal stress difference coefficient in the steady shear flow

$$\psi_1(\dot{\gamma}) = \frac{2n'\eta_0^{1+1/n'}}{(\eta_0/G_N^0)^{1/n'} [1 + (\eta_0\dot{\gamma}/G_N^0)^\alpha]^{n'+1}} \quad (14)$$

(v) Shear viscosity in the steady shear flow

$$\eta(\dot{\gamma}) = \frac{\eta_0}{[1 + (\eta_0\dot{\gamma}/G_N^0)^\alpha]^{n'}} \quad (15)$$

(vi) The ratio of N_1 to τ_{12} for the free recoil and viscous heating in the low- and high-shear rate limits of the steady shear flow.

The ratio of N_1 to τ_{12} for the free recoil and viscous heating in the zero- and infinite-shear rates ($\dot{\gamma}=0$ and $\dot{\gamma}=\infty$) may be obtained from the following equations:

$$\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}=0} = \lim_{\dot{\gamma} \rightarrow 0} \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_{S.F} = \left(\frac{\psi_{10}\dot{\gamma}_0}{2\eta_0} \right)_{S.F} \quad (16)$$

$$\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}=\infty} = \lim_{\dot{\gamma} \rightarrow \infty} \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_{S.F} = \left(\frac{\psi_{1\infty}\dot{\gamma}_\infty}{2\eta_\infty} \right)_{S.F} \quad (17)$$

where η_0 , ψ_{10} , and $\dot{\gamma}_0$ represent the shear viscosity, the first normal stress difference coefficient and the shear rate in $\dot{\gamma} = 0$, η_∞ , $\psi_{1\infty}$, and $\dot{\gamma}_\infty$ represent the shear viscosity, the first normal stress difference coefficient and the shear rate in $\dot{\gamma} = \infty$. $G_N^0 = \rho RT/\bar{M}_e$, ρ is the density of polymeric melts, R is the gas constant, \bar{M}_e is the molecular mass between entanglement sites, n' and α are, respectively, the average constrained dimensional numbers of terminal and loop constituent chains in the long and short entanglement spaces.

(vii) Determination of the molecular parameters of η_0 , G_N^0 , n' , and α in the constitutive equations and material functions.

A new method for the determination of line parameters (η_0 , G_N^0 , n' , and α) has been proposed in previous work [10]. It was found that these linear parameters can be obtained from the following Eqs.(18) and (19) by a linear plotting method [10,12].

$$\ln \eta(\dot{\gamma}) = \frac{n'}{n'+1} \ln \psi_1(\dot{\gamma}) + \frac{n'}{n'+1} \ln \frac{G_N^0}{(2n')^{n'}} \quad (18)$$

$$\begin{aligned} \ln \left[\frac{d \ln (\eta/\psi_1)}{d \ln \dot{\gamma}} \frac{\eta}{\psi_1} \right] &= \alpha \ln \dot{\gamma} + \ln \frac{\alpha}{2n'} \\ &+ \left(\alpha - \frac{1}{n'} \right) \ln \frac{\eta_0}{G_N^0} \end{aligned} \quad (19)$$

Eqs.(18) and (19) show that η_0 , G_N^0 , n' , and α can be determined from the slopes and intercepts of the lines by plotting $\ln \eta$ against $\ln \psi_1$ and by plotting $\ln \left[\frac{d \ln (\eta/\psi_1)}{d \ln \dot{\gamma}} \frac{\eta}{\psi_1} \right]$ against $\ln \dot{\gamma}$.

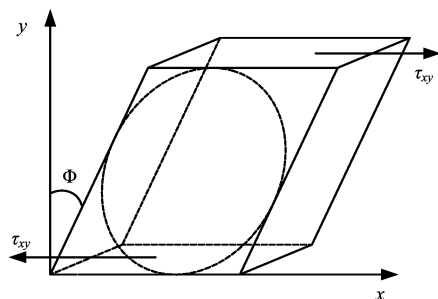


FIG. 1 The scheme of simple shear.

B. Correlation of the Ultimate free recoil to the molecular parameters and the operational variables after the steady shear flow and recoverable time

1. Partition function of the viscoelastic free (or constrained) recoil and the viscous heating for the entangled polymeric fluids

From Fig.1 [16] and Eq.(13) it is easy to show that the simple shear $\tan \Phi$ for the entangled polymeric liquids at $t_r = \infty$ may be represented by the shear strain, and it may be expressed as [1]

$$\begin{aligned} [S_{SR}(\infty)]_{S.F}^{\dot{\gamma}} &= (\tan \Phi)_{S.F}^{\dot{\gamma}} = \frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}} \\ &= \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_{S.F} \end{aligned} \quad (20)$$

In the simple shear flow the most important motions of polymeric liquids are the co-operative mode motion, which may be resolved into two correlative components: “local” (or micro-Brownian) and “normal” (or displacement of center mass) mode motions as shown in Fig.2 [17].

As shown in Eq.(20), the simple shear of the entangled polymeric liquids is the function of ratio $\psi_1(\dot{\gamma})$ to $\eta(\dot{\gamma})$ and $\dot{\gamma}$. The cooperation quantity $\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} = \tan \Phi$ can be used to couple the coexistence of free recoil with viscous heating of the polymeric liquids following the simple shear flow at steady $\dot{\gamma}$. Therefore we define the quantity $\tan \Phi$ as the cooperation function of “local” and “normal” mode motion in the unsteady $\dot{\gamma}$ and also define it as the partition function of the elastic free recoil and the viscous heating in the simple shear flow at the steady shear rate. We do this to distinguish the contribution of the free recoil and the viscous heating to $\tan \Phi$ in steady $\dot{\gamma}$. The following two exponential correlation parameters $1 - \overline{W}_{\dot{\gamma}}$ and $\overline{W}_{\dot{\gamma}}$ are introduced in order to measure the degree of contribution for the free recoil and the viscous heating to the $\tan \Phi$: (i) $1 - \overline{W}_{\dot{\gamma}}$ is the fraction of the recoverable conformation on the entangled polymeric chain (or at entangled state) in the polymeric fluids at the state of $\dot{\gamma}$ and L/D for a capillary; (ii) $\overline{W}_{\dot{\gamma}}$ is the fraction of the unrecoverable con-

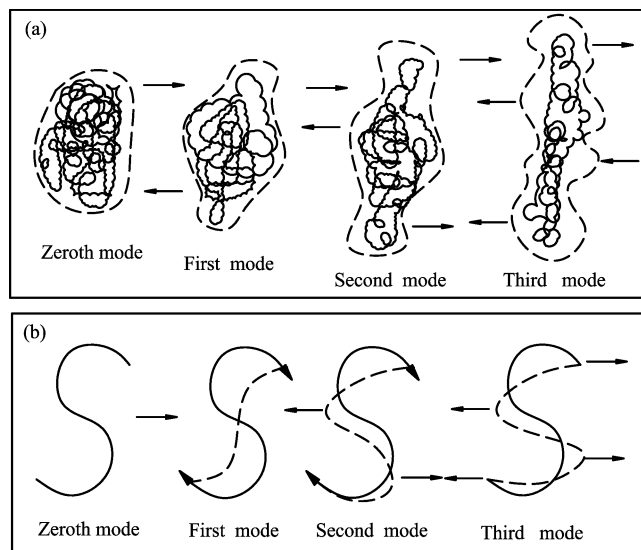


FIG. 2 The role of cooperative mode motions for “Local” and “Normal” mode relaxation of a polymer molecule may be expressed and compared in (a) and (b): The zeroth mode corresponds to the simple diffusion of the whole molecule, higher modes correspond to a cooperative diffusion of one part of the molecule relative to the remainder. For the first mode there is one mode produced, higher order modes lead to a corresponding increase in the number of modes.

formation on the disentangled polymeric chain (or at isolated state) in the polymeric fluids at $\dot{\gamma}$ and L/D for a capillary.

The fraction $1 - \overline{W}_{\dot{\gamma}}$ is defined as the ratio of the number for the recoverable conformation on the entangled polymeric chains to the total numbers of the recoverable and unrecoverable conformations on the entangled and disentangled polymeric chains in the polymeric fluids at steady $\dot{\gamma}$ and L/D for a capillary. The magnitude of the $1 - \overline{W}_{\dot{\gamma}}$ decrease with increasing $\dot{\gamma}$ and L/D for a capillary and increase with increasing the recoverable time t_r . The fraction $\overline{W}_{\dot{\gamma}}$ is defined as the ratio of the number for the unrecoverable conformation on the disentangled polymeric chains to the total numbers of the recoverable and unrecoverable conformations on the entangled and disentangled polymeric chains in the polymeric fluids at steady $\dot{\gamma}$ and L/D for a capillary. The magnitudes of the $\overline{W}_{\dot{\gamma}}$ increase with increasing $\dot{\gamma}$ and L/D for a capillary. Thus they must satisfy the following normalized condition:

$$\begin{aligned} (1 - \overline{W}_{\dot{\gamma}}) + \overline{W}_{\dot{\gamma}} &= 1 \\ \dot{\gamma}_0 \leq \dot{\gamma} \leq \dot{\gamma}_w, \quad (L/D)_0 \leq (L/D) \leq (L/D)_\infty \end{aligned} \quad (21)$$

Introducing the normalized condition of Eq.(21) into the partition function of the viscoelastic free recoil and

viscous heating, we have

$$\frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}} = [(\tan \Phi)^{(1-\bar{W}_{\dot{\gamma}})+\bar{W}_{\dot{\gamma}}}]_{S.F}^{\dot{\gamma}} = \left\{ \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]^{(1-\bar{W}_{\dot{\gamma}})+\bar{W}_{\dot{\gamma}}} \right\}_{S.F} \quad (22)$$

$$\frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}} = [(\tan \Phi)^{(1-\bar{W}_{\dot{\gamma}})+\bar{W}_{\dot{\gamma}}}]_{S.F}^{\dot{\gamma}} = \left\{ \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_E^{1-\bar{W}_{\dot{\gamma}}} \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_V^{\bar{W}_{\dot{\gamma}}} \right\}_{S.F} = [S_{URVT}(\infty)]_{S.F}^{\dot{\gamma}} [S_{VH}(\infty)]_{S.F}^{\dot{\gamma}} \quad (23)$$

Eq.(22) represents the grand partition function of the recoil and viscous heating resulting from both the micro-Brownian motion of segments and the displacement of mass center of the polymeric chains in the polymeric fluids at $t_r=\infty$. Eq.(22) and (23) shows that the partition function of the viscoelastic free recoil and viscous heating may be resolved into two correlation components

$$[(\tan \Phi)_E^{1-\bar{W}_{\dot{\gamma}}}]_{S.F}^{\dot{\gamma}} = [S_{URVT}(\infty)]_{S.F}^{\dot{\gamma}} = \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_E^{1-\bar{W}_{\dot{\gamma}}} \quad (24)$$

$$[(\tan \Phi)_V^{\bar{W}_{\dot{\gamma}}}]_{S.F}^{\dot{\gamma}} = [S_{VH}(\infty)]_{S.F}^{\dot{\gamma}} = \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_V^{\bar{W}_{\dot{\gamma}}} \quad (25)$$

Eq.(24) represents the ultimate recoverable shear strain resulting from the micro-Brownian motion of segments in the constituent chain at $t_r=\infty$, Eq.(25) represents the unrecoverable viscous heating (or viscous dissipation loss) resulting from the displacement of mass center for polymeric chain in the polymeric fluids at $t_r=\infty$.

2. Variation of ultimate recoverable viscoelastic strain and unrecoverable viscous heating at the very different $\dot{\gamma}$ and $t_r=\infty$ with $1 - \bar{W}_{\dot{\gamma}}$ and $\bar{W}_{\dot{\gamma}}$

The variation of $[S_{URVT}(\infty)]_{S.F}^{\dot{\gamma}}$ and $[S_{VH}(\infty)]_{S.F}^{\dot{\gamma}}$ with $1 - \bar{W}_{\dot{\gamma}}$ and $\bar{W}_{\dot{\gamma}}$ have been studied in a previous paper [14]. It was found that the entangled polymeric liquids under the different states of $\dot{\gamma}$ and L/D may exhibit the following very different viscoelastic behaviors: (i) Perfectly elastic behavior: For a given L/D , when $\dot{\gamma}=-dv/d\gamma=\dot{\gamma}_W$ approaches zero, then the value of $1 - \bar{W}_{\dot{\gamma}}$ will approach unity and the value of $\bar{W}_{\dot{\gamma}}$ will approach zero. Thus the entangled polymeric liquids may be converted to a perfectly entangled network and

Eq.(23) may reduce to

$$\frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}_W} = [(\tan \Phi)_E]_{S.F}^{\dot{\gamma}_W} = \left[\left(\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right)_E \right]_{S.F} = [S_{URVT}(\infty)]_{S.F}^{\dot{\gamma}_W} = \left[\left(\frac{\psi_{10}\dot{\gamma}_0}{2\eta_0} \right)_E \right]_{S.F} \quad (26)$$

This means that the polymeric liquids may exhibit a perfectly elastic behavior, and the expression of $\left[\left(\frac{\psi_{10}\dot{\gamma}_0}{2\eta_0} \right)_E \right]_{S.F}$ is completely identified with the expression of Bird [18].

(ii) Perfectly viscous behavior: For a given L/D , when $\dot{\gamma}=-dv/d\gamma=\dot{\gamma}_{\gamma=0}$ approaches maximum or infinite value, then the value $\bar{W}_{\dot{\gamma}}$ will approach unity and the value of $1 - \bar{W}_{\dot{\gamma}}$ will also approach zero, thus, the entangled polymeric liquids may be converted to a perfectly isolated polymeric chain liquids and Eq.(23) may reduce to

$$\frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}_{\gamma=0}} = [(\tan \Phi)_V]_{S.F}^{\dot{\gamma}_{\gamma=0}} = \left[\left(\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right)_{VH} \right]_{S.F} = [S_{VH}(\infty)]_{S.F}^{\dot{\gamma}_{\gamma=0}} = \left[\frac{\psi_{1\infty}\dot{\gamma}_{\infty}}{2\eta_{\infty}} \right]_{S.F} \quad (27)$$

This means that the polymeric liquids may exhibit perfectly viscous behavior.

(iii) Iso-viscoelastic (or linear viscoelastic) behavior: For a given L/D , when $\dot{\gamma}=-dv/d\gamma=\dot{\gamma}_{ISO}$ approaches zero and a maximum (or infinite) value, then the values of $1 - \bar{W}_{\dot{\gamma}}$ and $\bar{W}_{\dot{\gamma}}$ will approach 1/2. Thus, Eq.(23) reduces to

$$\frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}=\dot{\gamma}_0/2=\dot{\gamma}_{\infty}/2} = [(\tan \Phi)_E^{1/2} (\tan \Phi)_V^{1/2}]_{S.F}^{\dot{\gamma}=\dot{\gamma}_0/2=\dot{\gamma}_{\infty}/2} = \left\{ \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_E^{1/2} \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_V^{1/2} \right\}_{S.F}^{\dot{\gamma}=\dot{\gamma}_0/2=\dot{\gamma}_{\infty}/2} = [S_{URVT}(\infty)]_{S.F}^{\dot{\gamma}=\dot{\gamma}_0/2} [S_{VH}(\infty)]_{S.F}^{\dot{\gamma}=\dot{\gamma}_{\infty}/2} \quad (28)$$

This means that the entangled polymeric liquids may exhibit the iso-viscoelastic behaviors, where $\dot{\gamma}_{ISO}$ represents the critical shear rate at which the entangled polymeric liquids may exhibit the iso-viscoelastic (or linear viscoelastic) behaviors. This can be seen in Table I for all samples with $\langle 1 - \bar{W}_{\dot{\gamma}} \rangle = 0.505-0.514$.

TABLE I Molecular parameters of linear viscoelasticity for HDPE

Parameters	Figures (200 °C)	HDPE (220 °C)
$\eta/\text{Pa}\cdot\text{s}$	1.16×10^5	1.20×10^5
G_N^0/Pa	2.0×10^4	1.7×10^4
α	0.84	0.89
n'	0.84	0.81
$\langle 1 - \overline{W}_{\dot{\gamma}} \rangle$	0.505	0.514
$\langle \overline{W}_{\dot{\gamma}} \rangle$	0.495	0.486

(iv) No-iso (or No-linear)-viscoelastic behavior:

For a given L/D , when $\dot{\gamma} = -dv/d\dot{\gamma} > \dot{\gamma}_{\text{ISO}}$ (or $< \dot{\gamma}_{\text{ISO}}$) approaches zero and maximum (or infinite) values, then the values of $1 - \overline{W}_{\dot{\gamma}}$ and $\overline{W}_{\dot{\gamma}}$ may converge to particular values. Thus Eq.(22) reduces to

$$\begin{aligned} \frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}} &= \left\langle (\tan \Phi)_E^{1-\overline{W}_{\dot{\gamma}}} (\tan \Phi)_V^{\overline{W}_{\dot{\gamma}}} \right\rangle_{S.F}^{\dot{\gamma}} \\ &= \left\langle \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_E^{1-\overline{W}_{\dot{\gamma}}} \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_V^{\overline{W}_{\dot{\gamma}}} \right\rangle_{S.F}^{\dot{\gamma}} \\ &= \left\langle [S_{\text{URVT}}(\infty)]_{S.F}^{\dot{\gamma}} [S_{\text{VH}}(\infty)]_{S.F}^{\dot{\gamma}} \right\rangle \quad (29) \end{aligned}$$

This means that the polymeric liquids may exhibit the no-iso (or no-linear)-viscoelastic behavior. When $(1 - \overline{W}_{\dot{\gamma}}) > \overline{W}_{\dot{\gamma}}$, it exhibits the elastoviscous behavior, and $(1 - \overline{W}_{\dot{\gamma}}) < \overline{W}_{\dot{\gamma}}$, it exhibits viscoelastic behavior. Here ψ_{10} and $\psi_{1\infty}$ represent the first normal stress difference coefficients at the shear rate $\dot{\gamma}_W$ and $\dot{\gamma}_{\gamma=0}$ on the wall surface and at the center of the capillary.

These elastic-viscous $(1 - \overline{W}_{\dot{\gamma}}) > 1/2$ and viscoelastic $(1 - \overline{W}_{\dot{\gamma}}) < 1/2$ behaviors for each single and whole samples can be seen in Table II.

3. Conformational distribution in the ultimate free recoil

When the flow is suddenly stopped at an instant time; and no further flows take place, we know that the free energy ΔF_{ET} and the stress components will ultimately become isotropic. The rate or time variations for ΔF_{ET} , $\tau_{11} - \tau_{22}$, and τ_{12} in general have different values at different start of relaxation. Therefore, ΔF_{ET} , τ_{11} , τ_{22} , τ_{12} , and $\frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{\dot{\gamma}}$ must relax at very different rates.

According to the structural model of transition, the entanglement network and the multiple-repetition mechanism of polymeric chains are explained by the dynamic reorganization of entanglement sites. It is easy to distinguish the two types of molecular process, which proceed with a very different rate of relaxation. They may be characterized by the following two molecular processes: (i) The processes of loss and creation of the

entanglement sites between the polymeric chains or segments with gauche-form conformation f and the processes of reslipping of the segments with f in the entangled constituent chains, which are slow processes and are taken to be delayed; (ii) The process of the rearrangement for the population conformation from transform $1 - f$ to f on the extending segment of constituent chains, which is a fast process and is taken to be instantaneous. The two types of molecular process proceeding at very different rates of relaxation can be characterized by the expression of $\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W$ and the fractions of the recoverable and unrecoverable conformations on the entangled and disentangled polymeric chains in the polymeric fluids, $1 - \overline{W}_{\dot{\gamma}}$ and $\overline{W}_{\dot{\gamma}}$.

Therefore, in the simple shear flow the total recoverable viscoelastic recoil $[S_{\text{URVT}}(\infty)]_{S.F}^{\dot{\gamma}}$ in steady $\dot{\gamma}$ and recoverable time $t_r = \infty$ may be expressed as

$$\begin{aligned} \left[\frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_E^{1-\overline{W}_{\dot{\gamma}}} \right]_{S.F}^{\dot{\gamma}} &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} \\ &= \left\{ \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_E^{1-\overline{W}_{\dot{\gamma}}} \right\}_{S.F}^{\dot{\gamma}} = [S_{\text{URVT}}(\infty)]_{S.F}^{\dot{\gamma}} \quad (30) \end{aligned}$$

When the shear rate on the wall surface of capillary ($\dot{\gamma}_W = -dv/dr$) approaches zero, where dv/dr is the velocity gradient and $v=0$, then, the fraction of the recoverable conformation on the entangled polymeric chain $1 - \overline{W}_{\dot{\gamma}}$ will also approach unity [$(1 - \overline{W}_{\dot{\gamma}}) \approx 1$]. Thus, the total (or ultimate) recoverable viscoelastic strain for the entangled constituent chain following a steady shear flow is usually defined as the ratio of the first normal stress difference $(N_1)_W$ on the wall surface to shear stress $(\tau_{12})_W$ on the double surfaces of capillary under releasing stress

$$\begin{aligned} \left[\frac{1}{2} \left(\frac{\tau_{11} - \tau_{22}}{\tau_{12}} \right)_{S.F}^{1-\overline{W}_{\dot{\gamma}}} \right]_E^{\dot{\gamma}} &= \left[(\tan \Phi)_E^{1-\overline{W}_{\dot{\gamma}}} \right]_{S.F}^{\dot{\gamma}} \\ &= \left\{ \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]_E^{1-\overline{W}_{\dot{\gamma}}} \right\}_{S.F}^{\dot{\gamma}} = \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} \\ &= [S_{\text{URVT}}(\infty)]_{S.F}^{\dot{\gamma}} = \left[\left(\frac{\psi_{10}\dot{\gamma}_0}{2\eta_0} \right)_E \right]_{S.F}^{\dot{\gamma}} \quad (31) \end{aligned}$$

Eq.(31) shows that $1 - \overline{W}_{\dot{\gamma}}$ must approach unity for a perfectly entangled network. The expression of $\left[\left(\frac{\psi_{10}\dot{\gamma}_0}{2\eta_0} \right)_E \right]_{S.F}^{\dot{\gamma}}$ is completely identified with the expression of Bird [18].

The correlation of $\left[\frac{1}{2} \left(\frac{N_1}{\tau} \right)_W \right]_{S.F}^{\dot{\gamma}}$ to $[S_{\text{URVT}}(\infty)]_{S.F}^{\dot{\gamma}}$ and $[S_{\text{IRET}}(0)]_{S.F}^{\dot{\gamma}}$ has been deduced in the previous paper [14]. It was found that they may be characterized by the following relations: (i) The instantaneous recoverable strain in steady $\dot{\gamma}$

TABLE II Experimental data for HDPE

<i>L/D</i>	200 °C				220 °C			
	$\dot{\gamma}/S^{-1}$	<i>B</i> _{Exp}	$1 - \overline{W}_{\dot{\gamma}}$	$1-f$	$\dot{\gamma}/S^{-1}$	<i>B</i> _{Exp}	$1 - \overline{W}_{\dot{\gamma}}$	$1-f$
8					42.25	1.9166	0.5763	0.4537
					95.06	2.0923	0.5307	0.4640
					147.80	2.1919	0.5100	0.4683
					196.70	2.2640	0.4991	0.4709
					249.50	2.3147	0.4885	0.4725
16	46.28	1.7385	0.5618	0.4374	48.65	1.7492	0.5637	0.4387
	102.60	1.8319	0.4963	0.4470	107.60	1.9053	0.5213	0.4529
	163.40	1.9483	0.4866	0.4559	165.10	1.9285	0.4819	0.4546
	218.30	2.0010	0.4739	0.4592	224.10	1.9405	0.4565	0.4554
	277.60	2.0558	0.4669	0.4622	272.70	2.0357	0.4656	0.4611
24	387.50	2.1690	0.4654	0.4673	398.10	2.1647	0.4644	0.4672
	46.27	1.6602	0.5696	0.4271	48.28	1.6984	0.5943	0.4325
	104.10	1.8063	0.5227	0.4446	105.30	1.7926	0.5215	0.4433
	159.00	1.8622	0.4939	0.4495	162.40	1.8470	0.4912	0.4483
	211.10	1.9282	0.4863	0.4545	222.30	1.9242	0.4845	0.4543
32	263.20	1.9433	0.4692	0.4556	392.10	2.0383	0.4639	0.4612
	368.10	2.0464	0.4674	0.4617				
	45.84	1.5993	0.5717	0.4171	44.91	1.6318	0.6124	0.4227
	101.73	1.7580	0.5350	0.4397	98.00	1.7314	0.5360	0.4366
	173.30	1.8211	0.4944	0.4460	152.40	1.8517	0.5298	0.4487
40	209.10	1.8802	0.4954	0.4510	201.40	1.8745	0.5045	0.4505
	260.70	1.9303	0.4888	0.4547	255.80	1.9521	0.5044	0.4561
	382.50	2.0028	0.4729	0.4593	366.10	2.0082	0.4845	0.4596
	46.08	1.6018	0.6093	0.4175	47.22	1.6242	0.6378	0.4214
	100.80	1.6891	0.5267	0.4312	98.74	1.7187	0.5573	0.4351
78.7	156.90	1.7659	0.5047	0.4405	158.80	1.7912	0.5238	0.4431
	210.20	1.8012	0.4849	0.4441	206.00	1.8423	0.5122	0.4479
	260.60	1.8636	0.4850	0.4497	253.30	1.9155	0.5147	0.4536
					377.80	1.9611	0.4863	0.4567
	25.56	1.3755	0.6726	0.3511	40.24	1.4140	0.6134	0.3673
78.7	47.10	1.4117	0.5388	0.3664	49.50	1.3658	0.4895	0.3465
	67.28	1.4431	0.4996	0.3779	53.65	1.4167	0.5396	0.3684
	104.90	1.4922	0.4700	0.3929	88.52	1.4820	0.5071	0.3901
	160.10	1.5556	0.4577	0.4084	119.30	1.5222	0.4911	0.4007
	188.40	1.5764	0.4505	0.4127	144.80	1.5382	0.4740	0.4045
	234.10	1.6297	0.4555	0.4224	201.20	1.5843	0.4606	0.4143
	275.80	1.6435	0.4442	0.4246	228.00	1.6004	0.4548	0.4173

and $t_r=0$

$$\begin{aligned}
 [S_{\text{IRET}}(0)]_{S.F}^{\dot{\gamma}} &= [S_{\text{URVT}}(\infty)]_{S.F}^{\dot{\gamma}} (1 - f_e) \\
 &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} (1 - f_e) \\
 &= \left[\left(\frac{\psi_1(\dot{\gamma}) \dot{\gamma}}{2\eta(\dot{\gamma})} \right)^{1-\overline{W}_{\dot{\gamma}}} \right]_{S.F} (1 - f_e) \quad (32)
 \end{aligned}$$

(ii) The delayed recoverable viscoelastic strain (or viscoelastic recoil) in steady $\dot{\gamma}$ and $t_r = \infty$

$$\begin{aligned}
 [S_{\text{DRVT}}(\infty)]_{S.F}^{\dot{\gamma}} &= [S_{\text{URVT}}(\infty)]_{S.F}^{\dot{\gamma}} f_e \\
 &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} f_e \\
 &= \left[\left(\frac{\psi_1(\dot{\gamma}) \dot{\gamma}}{2\eta(\dot{\gamma})} \right)^{1-\overline{W}_{\dot{\gamma}}} \right]_{S.F} f_e \quad (33)
 \end{aligned}$$

Here $1-f_e$ is a time-independent fraction of trans-form conformations in the constituent chains which will take part in the rearrangement of the population conformation at the beginning of $t_r=0$. The expression $f_e=f(0)n_T\mu_0 \ln(t_\infty/t_0)$ is the fraction of gauche-form conformations on each disentangled polymeric chain which take part in the reorganization of entanglement sites at the recoverable time which approaches the infinite $t_r=\infty$; its value is a limited constant. In the expression, t_0 is the extrapolated initial time, n_T is the total numbers of disentanglement polymer chains to be taken part in the reorganization of constituent chains per unit volume, μ_0 is the reformation rate constant for the entangled constituent chain on each disentangled polymeric chain, and $f(0)$ is a critical fraction of gauche-form conformation existing in the polymeric fluids at the beginning of the recoverable time. Therefore, in the course of recovery there are a series of rearrangements of population conformation and the reentanglement of constituent chains will occur until they approach the equilibrium state.

(iii) The ultimate recoverable viscoelastic strain (or ultimate viscoelastic recoil) in steady $\dot{\gamma}$ and $t_r = \infty$

This may be expressed as the sum of its components [1]. Thus, we have

$$\begin{aligned} [S_{URVT}(0)]_{S.F}^{\dot{\gamma}} &= [S_{IRET}(0)]_{S.F}^{\dot{\gamma}} + [S_{DRVT}(\infty)]_{S.F}^{\dot{\gamma}} \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F} [(1-f_e) + f_e] \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F} \\ &= \left\{ \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]^{1-\bar{W}_{\dot{\gamma}}} \right\}_{S.F} \end{aligned} \quad (34)$$

4. Correlation of the ultimate free recoil to the molecular parameters and the operational variables

From Eq.(13), it is easy to determine that the function may be expressed as

$$\left\{ \left[\frac{\psi_1(\dot{\gamma})\dot{\gamma}}{2\eta(\dot{\gamma})} \right]^{1-\bar{W}_{\dot{\gamma}}} \right\}_{S.F} = \left[\frac{n'(\eta_0/G_N^0)^{1/n'}\dot{\gamma}}{1 + (\eta_0\dot{\gamma}/G_N^0)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \quad (35)$$

By substituting Eq.(35) into Eq.(34), the following equation is obtained:

$$\left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F} = \left[\frac{n'(\eta_0/G_N^0)^{1/n'}\dot{\gamma}}{1 + (\eta_0\dot{\gamma}/G_N^0)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \quad (36)$$

The key dimensionless parameter D_e [18] is usually defined as the ratio of a characteristic time τ of fluids to

a characteristic time t_f of the flow system. In the capillary, if the flow following a material particle is steady, then D_e may be also expressed as [18]

$$D_e = \tau\dot{\gamma} = \tau \frac{\langle \bar{v} \rangle}{D} \quad (37)$$

By introducing the relation $\tau = \eta_0/G_N^0$, the above equation may be rewritten as

$$\frac{\eta_0}{G_N^0}\dot{\gamma} = \tau\dot{\gamma} = \tau \frac{\langle \bar{v} \rangle}{D} = D_e \quad (38)$$

where D is the diameter of capillary and $\langle \bar{v} \rangle$ is the average flowing velocity in the capillary. For a given diameter, the average flow velocity $\langle \bar{v} \rangle$ may be characterized by a fractional length of that capillary per unit time, so $\langle \bar{v} \rangle$ may be expressed as $\langle \bar{v} \rangle = L/t_f$. Thus we have $L = t_f \langle \bar{v} \rangle$, where L is the length of capillary. Therefore, the Deborah number may be also expressed as

$$D_e = \frac{\eta_0}{G_N^0}\dot{\gamma} = \frac{\tau}{t_f} \frac{L}{D} \quad (39)$$

After introducing the dynamic equilibrium ratio of τ to t_f for the entangled polymeric chain to be disentangled in the steady shear rate, which is equal to unity $\tau/t_f=1$, then the above relation reduces to

$$\frac{\eta_0}{G_N^0}\dot{\gamma} = D_e = \frac{L}{D} \quad (40)$$

Substituting Eq.(40) into Eq.(36) the following equation is obtained:

$$\left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F} = \left[\frac{n'(\eta_0/G_N^0)^{1/n'}\dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \quad (41)$$

C. Correlation of the ultimate die swelling effect to the molecular parameters and the operational variables

1. Characteristics of recoverable viscoelastic free energy of deformation for the extrudates after releasing stress at the recoverable time

There are three kinds of the dynamic segments and chains with different fractions of $1-f_e$ and f_e in Eqs.(32) and (33), After removal of the stress, each kind of polymeric segment and chain with different $1-f_e$ and f_e fractions of trans- and gauche- form conformation will undergo a rearrangement of the conformation populations, the reslipping movement of the segments in entangled constituent chains, and the reorganization of entangled constituent chains between polymeric chains.

Therefore, from Eqs.(2) and (3), it is easy to show that for a small deformation the first order approximate

expression ΔF_{ET}^0 may be written as

$$\begin{aligned}\Delta F_{ET}^0 &= \Delta F_{TT} - (E_{VT} + C_{200}I_3) \\ &= G_{100E}^0 I_1 + G_{020EV}^0 I_2\end{aligned}\quad (42)$$

$$G_{100E}^0 = N_T C(t-t')^{n'-1} e^{-u(t-t')} C_{100E} \quad (43)$$

$$\begin{aligned}G_{020EV}^0 &= N_T C(t-t')^{n'-1} e^{-u(t-t')} \\ &\cdot (C_{020E} + C_{020V})\end{aligned}\quad (44)$$

They contribute to the instantaneous recoverable elastic free energy and the delayed recoverable viscoelastic free energy at steady $\dot{\gamma}$ and $t_r = \infty$, C_{100E} and C_{020V} is defined as the storage and loss modulus contributed by the different extending elastic segments and from the slipping segments and polymeric chains at different slipping state.

2. Characteristics of recoverable viscoelastic strain

Because the difference of ΔF_{ET}^0 satisfies the conditions of an exact differential, the partial derivatives of Eq.(42) with respect G_{100E}^0 and G_{020EV}^0 may be, respectively, defined as the instantaneous recoverable elastic strain $[S_{IRET}(0)]_{S.F}^{\dot{\gamma}}$ and the delayed recoverable viscoelastic strain $[S_{DRVT}(\infty)]_{S.F}^{\dot{\gamma}}$ in $\dot{\gamma}$, $t_r=0$ and $t_r=\infty$. Therefore, we have the following relations:

(i) Instantaneous recoverable elastic strain $t_r=0$

$$[S_{IRET}(0)]_{S.F}^{\dot{\gamma}} = I_1 = (\alpha_x^2 + \alpha_y^2 + \alpha_z^2) - 3 \quad (45)$$

(ii) Delayed recoverable viscoelastic strain at $t_r = \infty$

$$[S_{DRVT}(\infty)]_{S.F}^{\dot{\gamma}} = I_2 = \ln \left[\frac{1}{3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) \right] \quad (46)$$

(iii) Ultimate or total recoverable viscoelastic strain at $t_r = \infty$

$$\begin{aligned}[S_{URVT}(\infty)]_{S.F}^{\dot{\gamma}} &= [S_{IRET}(0)]_{S.F}^{\dot{\gamma}} + [S_{DRVT}(\infty)]_{S.F}^{\dot{\gamma}} \\ &= [(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) - 3] \\ &\quad + \ln \left[\frac{1}{3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) \right] \\ &= 2(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) - 5.098\end{aligned}\quad (47)$$

According to the conservation of the ultimate recoverable viscoelastic strain for the unconstrained recoil and the free die swell in the transient entanglement-network at a given steady $\dot{\gamma}$ and $t_r = \infty$, the following relations can be obtained from Eq.(47) (unconstrained recoil in steady shear flow and free die swell in the extrudate).

Therefore, Eq.(47) can be expressed as

$$\begin{aligned}2(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) - 5.098 \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right) \right]_{W,S.F} \\ &= \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}}\end{aligned}\quad (48)$$

3. Correlation of instantaneous and delayed recoverable strain to the fraction of recoverable conformation and the operational variables

The quantities of $[S_{IRET}(0)]_{S.F}^{\dot{\gamma}}$ and $[S_{DRVT}(\infty)]_{S.F}^{\dot{\gamma}}$ may be characterized by variables of (Eq.(41)) and the fraction of $1-f_e$ and f_e . Then from Eqs.(45) and (46), (47) and (32), (33) and (34), the following relations are obtained:

(i) Instantaneous recovery

$$\begin{aligned}[S_{IRET}(0)]_{S.F}^{\dot{\gamma}} &= \alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right) \right]_{W,S.F} (1 - f_e) \\ &= \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} (1 - f_e)\end{aligned}\quad (49)$$

(ii) Delayed recovery

$$\begin{aligned}[S_{DRVT}(\infty)]_{S.F}^{\dot{\gamma}} &= \ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3} \\ &= \alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 2.098 \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right) \right]_{W,S.F} f_e \\ &= \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} f_e\end{aligned}\quad (50)$$

(iii) Total recovery

$$\begin{aligned}[S_{URVT}(\infty)]_{S.F}^{\dot{\gamma}} &= [S_{IRET}(0)]_{S.F}^{\dot{\gamma}} + [S_{DRVT}(\infty)]_{S.F}^{\dot{\gamma}} \\ &= (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \\ &\quad + \ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3} \\ &= 2(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) - 5.098 \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right) \right]_{W,S.F} \\ &= \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}}\end{aligned}\quad (51)$$

D. A new set of equations on swelling effect and ratio

1. The state of deformation for B of extrudates

The state of deformation for swelling ratio B of extrudates may be considered as a uniform two-dimensional extension [16]. In this type of strain, the sample is stretched by equal amounts in two directions at right angles. The strain corresponds exactly with that in a

unidirectional compression; the only difference is the method of applying the stress. If the stretch ratio is α , we have

$$\alpha_x = \alpha_y = \alpha; \quad \alpha_z = \alpha^{-2} \quad (52)$$

After introducing Eq.(52) and the definition of swelling ratio ($B=D_f/D$ and $B=\alpha$) into Eqs.(49), (50), and (51), we get

$$\begin{aligned} [S_{\text{IRET}}(0)]_{S.F}^{\dot{\gamma}} &= \left(2B_{\text{IRET}}^2 + \frac{1}{B_{\text{IRET}}^4} - 3 \right) \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F} (1 - f_e) \\ &= (1 - f_e) \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \end{aligned} \quad (53)$$

$$\begin{aligned} [S_{\text{DRVT}}(\infty)]_{S.F}^{\dot{\gamma}} &= 2B_{\text{DRVT}}^2 + \frac{1}{B_{\text{DRVT}}^4} - 2.098 \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F} f_e \\ &= \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} f_e \end{aligned} \quad (54)$$

$$\begin{aligned} [S_{\text{IRET}}(0)]_{S.F}^{\dot{\gamma}} + [S_{\text{DRVT}}(\infty)]_{S.F}^{\dot{\gamma}} &= 4B_{\text{URVT}}^2 + \frac{2}{B_{\text{URVT}}^4} - 5.098 \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F} \\ &= \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \end{aligned} \quad (55)$$

where D and D_f are diameters of the tube and the extrudate.

2. A new equation for the instantaneous swelling effect and ratio

From Eq.(53), the correlation of swelling effect to $1 - f_e$, the operational variables $\dot{\gamma}$ and L/D and $t_r = 0$ may be expressed as

$$\begin{aligned} [S_{\text{IRET}}(0)]_{S.F}^{\dot{\gamma}} &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F} (1 - f_e) \\ &= 2B_{\text{IRET}}^2 + \frac{1}{B_{\text{IRET}}^4} - 3 \\ &= (1 - f_e) \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \end{aligned} \quad (56)$$

When $B_{\text{IRET}} \gg 1$, Eq.(44) tend to

$$2B_{\text{IRET}}^2 - 3 = \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} (1 - f_e) \quad (57)$$

Thus, B_{IRET} may be expressed as

$$B_{\text{IRET}} = \left\{ \frac{1}{2} \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \cdot (1 - f_e) + \frac{3}{2} \right\}^{1/2} \quad (58)$$

When $\left(\frac{N_1}{\tau_{12}} \right)_W \rightarrow 0$ or $\dot{\gamma} \rightarrow 0$ and $(L/D) \rightarrow \infty$, then B_{IRET} approaches to 1.22.

If $(1 - f_e) = 0.5$, then Eq.(58) can be reduced to

$$B_{\text{IRET}5} = \left\{ \frac{1}{4} \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} + \frac{3}{2} \right\}^{1/2} \quad (59)$$

Eq.(59) shows that this equation is a universal equation for characterizing the instantaneous swelling ratio in the extrudate.

3. A new equation on the ultimate swelling effect

From Eq.(55), the correlation of ultimate swelling effect in steady $\dot{\gamma}$ and $t_r = \infty$ to the operational variables ($\dot{\gamma}$ and L/D) may be expressed as

$$\begin{aligned} 4B_{\text{URVT}}^2 + \frac{2}{B_{\text{URVT}}^4} - 5.098 &= \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \end{aligned} \quad (60)$$

When $B_{\text{URVT}} \gg 1$, Eq.(60) tends to

$$4B_{\text{URVT}}^2 - 5.098 = \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \quad (61)$$

Thus, B_{URVT} may be expressed as

$$B_{\text{URVT}} = \left\{ \frac{1}{4} \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} + \frac{5.098}{4} \right\}^{1/2} \quad (62)$$

When $\left(\frac{N_1}{\tau_{12}} \right)_W \rightarrow 0$ or $\dot{\gamma} \rightarrow 0$ and $L/D \rightarrow \infty$, the B_{URVT} converges to about 1.13; the value of 0.13 is completely identical to the slow Newtonian flow [19].

Experimental results show that when the simple shear flows is performed in a narrow range of $\dot{\gamma}$ and L/D , and the variations of the fraction for the recoverable conformations $1 - \overline{W}_{\dot{\gamma}}$ with $\dot{\gamma}$ and L/D are very weak, then the average values of the fraction for $1 - \overline{W}_{\dot{\gamma}}$ may be approximately considered as constant. Therefore, the value of $1 - \overline{W}_{\dot{\gamma}}$ over the whole numbers of $\dot{\gamma}$ and L/D in the narrow range is expressed as $\langle 1 - \overline{W}_{\dot{\gamma}} \rangle = k$. Thus Eq.(62) reduces to

$$B_{URVT} = \left\{ \frac{1}{4} \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^k + \frac{5.098}{4} \right\}^{1/2} \quad (63)$$

When the average value of the fraction for recoverable conformations over the whole ranges of $\dot{\gamma}$ and L/D approaches 1/2, Eq.(63) reduces to

$$B_{URVT5} = \left\{ \frac{1}{4} \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1/2} + \frac{5.098}{4} \right\}^{1/2} \quad (64)$$

Eq.(64) shows that this equation is a universal equation for characterizing the ultimate swelling ratio in the extrudate at the iso-viscoelastic (or linear-viscoelastic) state $\langle 1 - \overline{W}_{\dot{\gamma}} \rangle = 1/2$. It can be seen in Fig.3(d).

III. A NEW SET OF GROWTH EQUATIONS ON THE EXTRUDATE SWELLING EFFECT AND RATIO UNDER THE FREE AND DYNAMIC STATES

A. Dynamics of the recovery (or growth) equation for the delayed recoil and recoverable viscoelastic strains

1. Repetition of segments and reorganization of entanglement sites on the disentangled polymeric chains

In the reverse direction of disentanglement of the entangled polymeric chains the repetition of polymeric chains and segments and the dynamically reversible reorganization of reentangled constituent chains on the disentangled polymeric chains is carried out with the following three steps: (i) Reentanglement of terminal constituent chains by Brown's thermal movement with a reformation rate constant $u_t = (G_N^0/\eta_0)^{1/n'}$. (ii) Reentanglement of middle loop constituent chains with a coupled reformation rate constant $u_l = u_t/u_d$: Theoretically, the reentanglement of the middle loop entanglement sites may be characterized by a reentanglement rate constant $u_d = (G_N^0/\eta_0 \dot{\gamma})^\alpha = 1/D_e^\alpha$, but in the real reformation of the transit network, there is a correlation between the terminal and loop segment relaxations in their adjacent constituent chains. Therefore, the real reentanglement of the middle loop constituent chains is not only determined by the magnitude of u_d , but also controlled by the magnitude of u_t . Thus,

$u_l = u_t/u_d = (G_N^0/\eta_0)^{1/n'} D_e^\alpha$ must be used to characterize the real reentanglements of middle loop entangled constituent chain; (iii) Total reentanglement of the entangled constituent chain on the each disentangled polymer chains with a total reformation rate constant $u_0 = u_t + u_l = (G_N^0/\eta_0)^{1/n'} (1 + D_e^\alpha)$.

2. Correlation of $u_0 = 1/\tau_0$ to the molecular parameters and the operational variables

Substituting Eq.(40) and the $\tau_{12} = \eta_0 \dot{\gamma}$ into the above equation, the following equations are obtained:

$$\begin{aligned} u_0 &= \frac{1}{\tau_0} = \left(\frac{G_N^0}{\eta_0} \right)^{1/n'} (1 + D_e^\alpha) \\ &= \left(\frac{G_N^0}{\eta_0} \right)^{1/n'} \left[1 + \left(\frac{\eta_0 \dot{\gamma}}{G_N^0} \right)^\alpha \right] \end{aligned} \quad (65)$$

$$\begin{aligned} u_0 &= \frac{1}{\tau_0} = \left(\frac{G_N^0}{\eta_0} \right)^{1/n'} (1 + D_e^\alpha) \\ &= \left(\frac{G_N^0}{\eta_0} \right)^{1/n'} \left[1 + \left(\frac{\tau_{12}}{G_N^0} \right)^\alpha \right] \end{aligned} \quad (66)$$

$$\begin{aligned} u_0 &= \frac{1}{\tau_0} = \left(\frac{G_N^0}{\eta_0} \right)^{1/n'} (1 + D_e^\alpha) \\ &= \left(\frac{G_N^0}{\eta_0} \right)^{1/n'} \left[1 + \left(\frac{L}{D} \right)^\alpha \right] \end{aligned} \quad (67)$$

Eqs.(65), (66), (67) can be successfully used to predict the correlations of $u_0 = 1/\tau_0$ to the molecular parameters and the operational variables.

3. Dynamics of the recovery (or growth) equation for the delayed free recoil and recoverable viscoelastic strains

It is easy to know that in the process of extrudate swell (or recoil) there are two types of molecular relaxation processes, one is the instantaneous molecular relaxation resulting in the reslipping of segments and the rearrangement of the population of conformations on the segments of constituent chains from the trans to gauche form; the other one is the delayed molecular relaxation resulting from the dynamic reorganization of entanglement sites between the disentanglement chains. Therefore, as the recoil and extrudate swelling proceeds, the rate of change in the quantities of delayed recoil $\left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S,F}^{\dot{\gamma}}$ and recoverable viscoelastic strains $\ln[(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)/3]$ is not only determined by the rate of change in the total numbers n_T of disentangled polymeric chains per unit volume to be taken part in the reorganization of entangled constituent chain over the

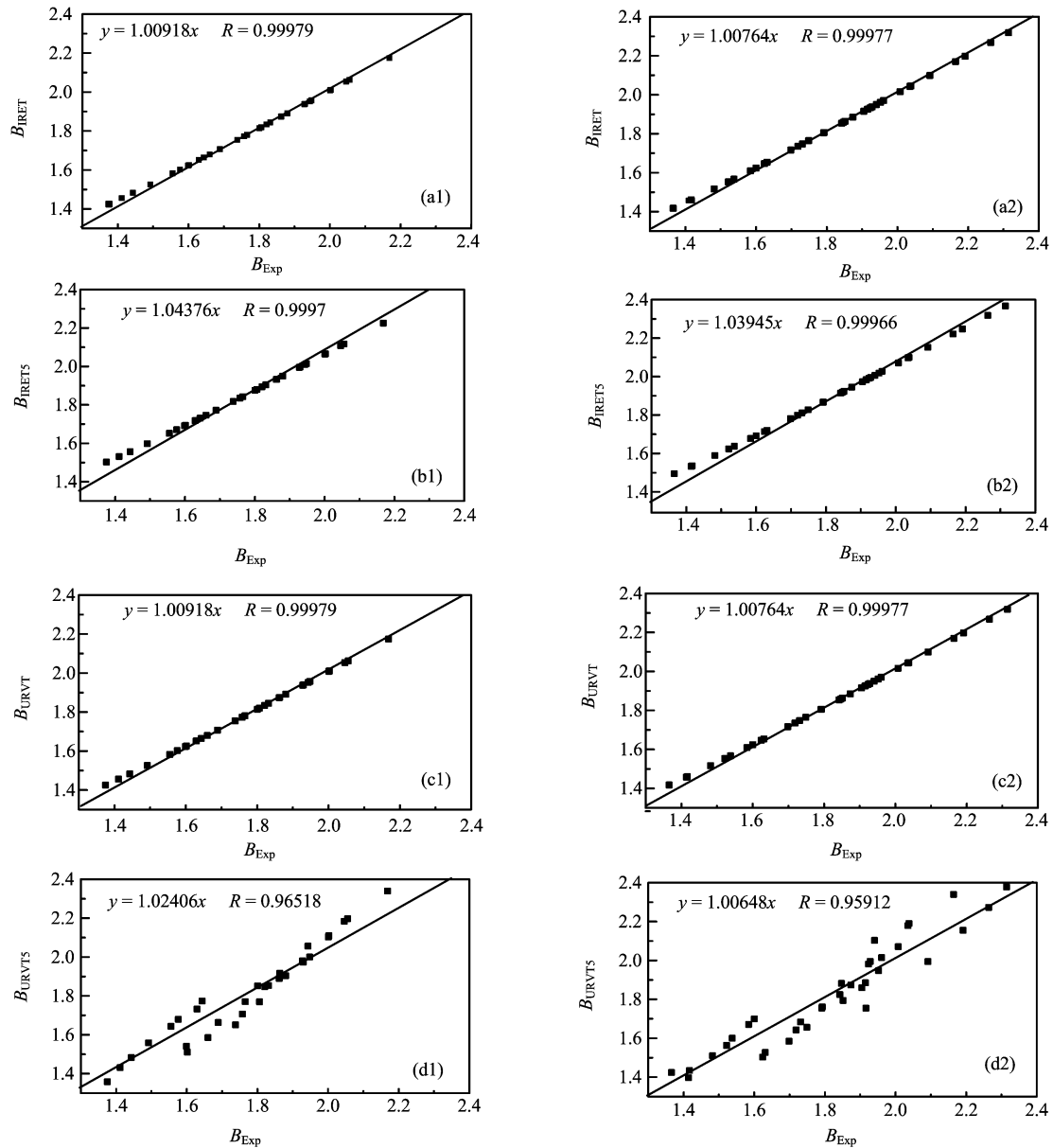


FIG. 3 Comparison of the theoretical values B_{IRET} from Eq.(58) (a), B_{IRET5} from Eq.(59) (b), B_{URVT} from Eq.(62) (d), and B_{URVT5} from Eq.(64) (d) with experimental data for HDPE at different temperatures ((1) $T=200$ °C and (2) $T=220$ °C) and different L/D and $\dot{\gamma}$.

time interval t (n_T/t), but also controlled by the reformation rate constant of the reentangled constituent chains on the each disentangled polymeric chains μ_0 . Therefore, their reformation rate may be characterized by the following equations:

$$\frac{d}{dt} \left\{ \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} f \right\} = u_0 \frac{n_T}{t} \quad (68)$$

$$\frac{d}{dt} \left[\ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3} \right] = u_0 \frac{n_T}{t} \quad (69)$$

After integrating and introducing the initial and final conditions of time ($t=0$ and $t=t$), we have

$$\left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} f(t) = \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} \cdot f(0) n_T \mu_0 \ln \frac{t}{t_0} \quad (70)$$

$$\ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3}(t) = \ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3}(0) n_T \mu_0 \ln \frac{t}{t_0} \quad (71)$$

Here $f(t)$ represents the fractions of gauche-form conformations to be reorganized for the entanglement sites

at the recoverable time, so $f(0)$ is a critical fraction of gauche-form conformations to be reorganized for the entanglement sites on the each disentangled polymeric chain at the front of beginning of $t_r=0$.

B. Correlation of the delayed recoverable viscoelastic strains to the molecular parameters, the operational variables and the recoverable time

By comparison of Eqs.(70) and (71), It is easy to obtain the following equation:

$$\begin{aligned} \ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3}(t) &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} f(t) \\ &= \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}} f(0)n_T\mu_0 \ln \frac{t}{t_0} \end{aligned} \quad (72)$$

After introducing the relationship between the $\left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_W \right]_{S.F}^{\dot{\gamma}}$ and the $\left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}}$ into the above equation, we get

$$\begin{aligned} \ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3}(t) &= \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} f(0)n_T\mu_0 \ln \frac{t}{t_0} \quad (73) \\ \ln \frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2}{3}(t) &= \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} f(0)n_T\mu_0 \ln \frac{t}{t_0} \quad (74) \end{aligned}$$

where $\tau_{12} = \eta_0 \dot{\gamma}$. The correlation of the delayed recoverable viscoelastic strains to the molecular parameters and the operation variables under the free and dynamic states was obtained.

C. Correlation of the delayed extrudate swelling effect to the molecular parameters, the operational variables and the recoverable time

1. The state of deformation of the delayed extrudate swelling ratio

The state of deformation for the delayed swell ratio $B_{DRVT}(t)$ in the extrudate was obtained by the same method. After introducing the definition of delayed swelling ratio in extrudate $B_{DRVT}(t)=D_f(t)/D$ [8], and then $B_{DRVT}(t)$ can be substituted into Eq.(54). The correlation of the delayed extrudate swelling effect to

the molecular parameters and the operational variables was obtained, and may be expressed as

$$\begin{aligned} 2B_{DRVT}^2(t) + \frac{1}{B_{DRVT}^4(t)} - 2.098 &= \left[\frac{n' (1/G_N^0)^{1/n'} (\eta_0)^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \\ &\cdot f(0)n_T\mu_0 \ln \frac{t}{t_0} \end{aligned} \quad (75)$$

where $D_f(t)=D'(t)$ is the diameter of delayed extrudate at $t_r=t$ [8], and D is the diameter of the tube (or capillary).

2. Growth equation on the delayed extrudate swelling ratio

Eq.(75) may be rewritten in the following forms:

$$\begin{aligned} B_{DRVT}^2(t) + \frac{1}{2B_{DRVT}^4(t)} &= 1.050 + \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \\ &\cdot \frac{f(0)n_T\mu_0}{2} (\ln t - \ln t_0) \end{aligned} \quad (76)$$

$$\begin{aligned} B_{DRVT}^2(t) + \frac{1}{2B_{DRVT}^4(t)} &= 1.050 + \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \\ &\cdot \frac{f(0)n_T\mu_0}{2} [2.303 (\lg t - \lg t_0)] \end{aligned} \quad (77)$$

When $2B_{DRVT}^2(t) \gg \frac{1}{B_{DRVT}^4(t)}$, then Eq.(75) may converge to

$$\begin{aligned} 2B_{DRVT}^2(t) &= \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_{\dot{\gamma}}} \\ &\cdot f(0)n_T\mu_0 \ln \frac{t}{t_0} + 2.098 \end{aligned} \quad (78)$$

Eq.(78) may be rewritten as

$$B_{\text{DRV T}}(t) = \left\{ \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \cdot \frac{f(0)n_T\mu_0 \ln t/t_0}{2} + 1.050 \right\}^{1/2} \quad (79)$$

$$B_{\text{DRV T}}(t) = \left\{ 1 + \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \cdot \frac{f(0)n_T\mu_0}{2 \times 1.050} \ln \frac{t}{t_0} \right\}^{1/2} (1.050)^{1/2} \quad (80)$$

By introducing

$$(1+x)^m = 1+mx \quad (m=1/2) \quad (81)$$

$$x = \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \cdot \frac{f(0)n_T\mu_0}{2 \times 1.050} \ln \frac{t}{t_0} \quad (82)$$

thus Eq.(80) may be approximately expressed as

$$B_{\text{DRV T}}(t) = \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \cdot \frac{f(0)n_T\mu_0}{4 \times (1.050)^{1/2}} \ln \frac{t}{t_0} + (1.050)^{1/2} \\ = 1.025 + A \ln \frac{t}{t_0} \quad (83)$$

$$A = \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \cdot \frac{f(0)n_T\mu_0}{4 \times (1.050)^{1/2}} \quad (84)$$

After introducing Eq.(67), we get

$$A = \frac{n'^{1-\bar{W}_\gamma} (1/G_N^0)^{\bar{W}_\gamma/n'} [1 + (L/D)^\alpha]^{\bar{W}_\gamma} \tau_{12}^{1-\bar{W}_\gamma}}{4 \times (1.050)^{1/2} \eta_0^{1+\bar{W}_\gamma(1/n'-1)}} \cdot f(0)n_T \quad (85)$$

For Iso-viscoelastic fluids $(1 - \bar{W}_\gamma) = 1/2$ and $\bar{W}_\gamma = 1/2$, and by introducing the relation $\bar{W}_\gamma = 1/2$ into the above relation, the expression of molecular parameter A may be re-expressed as

$$A_I = \frac{n'^{1/2} (1/G_N^0)^{1/2n'} [1 + (L/D)^\alpha]^{1/2} \tau_{12}^{1/2}}{4 \times (1.050)^{1/2} \eta_0^{[1/2(1+1/n')]} } \cdot f(0)n_T \quad (86)$$

where A and A_I represents the delayed extrudate swell growth rate. For a given polymeric system, the parameters of G_N^0 , η_0 , n' , α , $f(0)$, and n_T are all constants, thus, it is very easy to see how the parameters A vary with the operational conditions; For a given operational conditions (τ_{12} , $\dot{\gamma}$, and L/D), then the τ_{12} , $\dot{\gamma}$, and L/D are all constants, thus, it can be used to predict the correlation of parameter A to the primary structure of polymeric chains.

Eq.(83) may be rewritten as the other form:

$$B_{\text{DRV T}}(t) = 1.025 + 2.303A \lg(t/t_0) \quad (87)$$

Eq.(87) is completely identified with empirical equation of Wang [8]. It may be also rewritten by the following form:

$$B_{\text{DRV T}}(t) = 1.025 - 2.303A \lg t_0 + 2.303A \lg t \quad (88)$$

Because the values of t_0 is almost less than unity [8], then the value of $\lg t_0$ is also less than zero $\lg t_0 < 0$. Therefore, Eq.(88) may be rewritten as

$$B_{\text{DRV T}}(t) = 1.025 + 2.303A |\lg t_0| + 2.303A \lg t \\ = B_A + D_A \lg t \quad (89)$$

Eqs.(83) and (89) show that there are a linear correlations between the $B_{\text{DRV T}}(t)$ and $\ln t$ (or $\lg t$), and two kinds of lines may be obtained by plotting $B_{\text{DRV T}}(t)$ against $\ln t$ (or $\lg t$), the parameters D_A and B_A may be obtained from the slopes and intercepts of two lines, where $|\lg t_0|$ represents the absolute value to be taken.

D. A new set of equations on the delayed and total extrudate swelling ratios

1. A new equation on the delayed extrudate swelling ratio (DESR) at the recoverable (or growth) time

When $2B_{\text{DRV T}}^2(t) \gg 1/B_{\text{DRV T}}^4(t)$, Eq.(75) converges to

$$2B_{\text{DRV T}}^2(t) - 2.098 = \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{(1/n'-1)} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \cdot f(0)n_T\mu_0 \ln \frac{t}{t_0} \quad (90)$$

When $(1 - \bar{W}_\gamma) = 1/2$, then Eq.(90) reduces to

$$B_{\text{DRV T}}(t) = \left\{ \left[\frac{n' (1/G_N^0)^{1/n'} \eta_0^{(1/n'-1)} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1/2} \cdot \frac{f(0)}{2} n_T\mu_0 \ln \frac{t}{t_0} + 1.050 \right\}^{1/2} \quad (91)$$

2. A new equation on the total (or ultimate) extrudate swelling ratio (UESR) at the recoverable (or growth) time

From Eqs.(53), (54) and (55) it is easy to see that the total extrudate swelling effect under the free and dynamic states at $t_r=t$ may be also expressed as sum of the instantaneous extrudate swelling effect resulting from instantaneous recoverable elastic strains $\alpha_x^2+\alpha_y^2+\alpha_z^2-3$ and the delayed extrudate swelling effect resulting from the delayed recoverable viscoelastic strain $\ln[1/3(\alpha_x^2+\alpha_y^2+\alpha_z^2)]$. Thus, from Eqs.(53), (54) and (55) it is easily seen that the instantaneous, delayed and total extrudate swelling effects under the free and dynamic state at $t_r=t$ may be also expressed as

(i) The instantaneous extrudate swelling effect at $t_r=0$

$$\begin{aligned} & 2B_{\text{IRET}}^2(t_0) + \frac{1}{B_{\text{IRET}}^4(t_0)} - 3.0 \\ &= \left[1 - f(0)n_T\mu_0 \ln\left(\frac{t_\infty}{t_0}\right)_e \right] \\ & \cdot \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \\ &= (1-f_e) \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \end{aligned} \quad (92)$$

Eq.(92) shows that the instantaneous extrudate swelling effect results from the rearrangement of the population conformation of segments in the constituent chains.

(ii) The delayed extrudate swelling effect at $t_r=t$.

$$\begin{aligned} & 2B_{\text{DRV T}}^2(t) + \frac{1}{B_{\text{DRV T}}^4(t)} - 2.098 = f(0)n_T\mu_0 \ln\left(\frac{t}{t_0}\right) \\ & \cdot \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \end{aligned} \quad (93)$$

Eq.(93) shows that the delayed extrudate swelling effect results from the reslipping of segments and the reorganization of entanglement sites on the polymeric chains.

(iii) The total (or ultimate) extrudate swelling effect at the recoverable (or growth) time $t_r=t$.

$$\begin{aligned} & 4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 \\ &= \left[2B_{\text{IRET}}^2(t_0) + \frac{1}{B_{\text{IRET}}^4(t_0)} - 3.0 \right] \\ &+ \left[2B_{\text{DRV T}}^2(t) + \frac{1}{B_{\text{DRV T}}^4(t)} - 2.098 \right] \\ &= \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \\ & \cdot \left\{ \left[1 - f(0)n_T\mu_0 \ln\left(\frac{t_\infty}{t_0}\right)_e \right] + f(0)n_T\mu_0 \ln\frac{t}{t_0} \right\} \\ &= \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \\ & \cdot \left[(1-f_e) + f(0)n_T\mu_0 \ln\frac{t}{t_0} \right] \end{aligned} \quad (94)$$

where $f_e=f(0)n_T\mu_0 \ln(t_\infty/t_0)_e$, $t_r=\infty$. This is a limited fraction of gauche-form conformations at the recoverable time t_r that approached infinity $t_r=\infty$.

If $t_r=t=\infty$, then Eq.(94) reduces to the following form:

$$\begin{aligned} & 4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 = [(1-f_e) + f_e] \\ & \cdot \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \end{aligned} \quad (95)$$

When $4B_{\text{URVT}}^2(t) \gg \frac{2}{B_{\text{URVT}}^4(t)}$, then the above equation may be rewritten as in the following form:

$$\begin{aligned} & B_{\text{URVT}}(t) = \left\{ \frac{1}{4} \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \right. \\ & \left. + \frac{5.098}{4} \right\}^{1/2} \end{aligned} \quad (96)$$

When $(1-\bar{W}_\gamma)$ approaches 1/2, then Eq.(96) reduces to

$$\begin{aligned} & B_{\text{URVT}}(t) = \left\{ \frac{1}{4} \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1/2} \right. \\ & \left. + \frac{5.098}{4} \right\}^{1/2} \end{aligned} \quad (97)$$

Eqs.(96) and (97) show that when $t_r=t=\infty$, they may

be, respectively, rewritten as

$$B_{\text{URVT}}(\infty) = \left\{ \frac{1}{4} \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\dot{\gamma}} + \frac{5.098}{4} \right\}^{1/2} \quad (98)$$

$$B_{\text{URVT5}}(\infty) = \left\{ \frac{1}{4} \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1/2} + \frac{5.098}{4} \right\}^{1/2} \quad (99)$$

Eqs.(98) and (99) are completely identified with Eqs.(62) and (64) under the free and equilibrium states.

IV. VERIFICATION OF THE DYNAMIC THEORY OF DIE SWELL

A. Experimental results

The dependence of $\eta(\dot{\gamma})$ and $\psi_1(\dot{\gamma})$ on the shear rate $\dot{\gamma}$ [10] and the dependence of swelling ratio B in extrudates on the shear rate $\dot{\gamma}$ and the ratio of length L to diameter D for the linear polyethylene (HDPE) under the condition of flow stability have been studied by Chan *et al.* [20,21,22]. These results are given in Fig.3 (a), (b), (c), (d) and Tables I and II.

The dependence of dynamic extrudate swelling ratio $B_{\text{DRVT}}(t)$ on the function of $\lg(t/t_0)$ for linear polybutadiene(PBD) with the different molecular weight \bar{M}_W and a given \bar{M}_e (or concentration) at the different operational variables (τ_{12} , L/D , and dispersing medium) under the condition of flow stability have been studied by Wang [8]. These results are also given in Fig.4. These experimental methods and procedures are given in [8,20-22].

B. Determination of molecular parameters for HDPE

1. η_0 and α

Eq.(19) shows that a line can be obtained by plotting $\ln \left[\frac{d \ln (\eta/\psi_1)}{d \ln \dot{\gamma}} \frac{\eta}{\psi_1} \right]$ against $\ln \dot{\gamma}$, as given in Fig.3(d) and Fig.4(a) [12]. Then the parameters of η_0 and α for all samples can be determined from the slope and intercept of the lines with Eq.(19). Their values for all samples are given in Table I.

2. G_N^0 and n'

Eq.(18) shows that a line can be obtained by plotting $\ln \eta$ against $\ln \psi_1(\dot{\gamma})$ as shown in Fig.3(c) [12]. Then the

parameters G_N^0 and n' for all samples can be determined from the slope and intercept of the line with Eq.(18). Their values for all samples are given in Table I.

3. The fraction for recoverable conformation at the state of shear rate and recoverable time in extrudates

Taking the logarithm on both sides of Eq.(60), we get

$$1 - \bar{W}_\dot{\gamma} = \frac{\ln [4B_{\text{URVT}}^2 + 2/B_{\text{URVT}}^4 - 5.098]}{\ln \left\{ n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma} / [1 + (L/D)^\alpha] \right\}} \quad (100)$$

Eq.(100) shows that the fraction of recoverable conformations ($1 - \bar{W}_\dot{\gamma}$) for each sample at the state of $\dot{\gamma}$ and $t_r = \infty$ can be directly calculated from the swelling ratio $B_{\text{Exp}} = B_{\text{URVT}}$, n' , α , η_0 , and G_N^0 and the operating variables ($\dot{\gamma}$ and L/D). The value of $(1 - \bar{W}_\dot{\gamma})$ for each sample is given in Table II.

The average values of fraction for recoverable conformations over the whole number values of $\dot{\gamma}$ and L/D are also calculated with the following equations:

$$\langle 1 - \bar{W}_\dot{\gamma} \rangle = k = \sum_{l=1}^m \frac{\bar{A}_{\dot{\gamma}l}}{m} \quad (101)$$

$$\bar{A}_{\dot{\gamma}} = \sum_{i=1}^n \frac{1 - \bar{W}_{\dot{\gamma}i}}{n} \quad (102)$$

where the numbers of m and n are the whole numbers of L/D and $\dot{\gamma}$. The average values of $\langle 1 - \bar{W}_\dot{\gamma} \rangle$ over the whole numbers of $\dot{\gamma}$ and L/D for the HDPE at two different temperatures (200 and 220 °C) are, respectively, equal to 0.505 and 0.514, as shown in Table I. They show that their average values approach 1/2, or their average values are situated at the iso- or linear-viscoelastic state $\langle 1 - \bar{W}_\dot{\gamma} \rangle \approx 1/2$. Their die swelling behaviors may be approximately considered as an iso-die swelling behavior. This can be seen from Fig.3(d).

4. $1 - f$ in extrudates

Eq.(53) may be rewritten as

$$1 - f = \frac{2B_{\text{IRET}}^2 + 1/B_{\text{IRET}}^4 - 3}{\left\{ n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma} / [1 + (L/D)^\alpha] \right\}^{1-\bar{W}_\dot{\gamma}}} \quad (103)$$

Eq.(103) shows that the parameter of $1-f$ can be directly calculated from the molecular parameters (n' , α , η_0 , G_N^0 , and $1 - \bar{W}_\dot{\gamma}$), the swelling ratio ($B_{\text{Exp}} = B_{\text{URVT}}$) and the operating variables ($\dot{\gamma}$ and L/D). The values of $1-f$ for all samples are given in Table II.

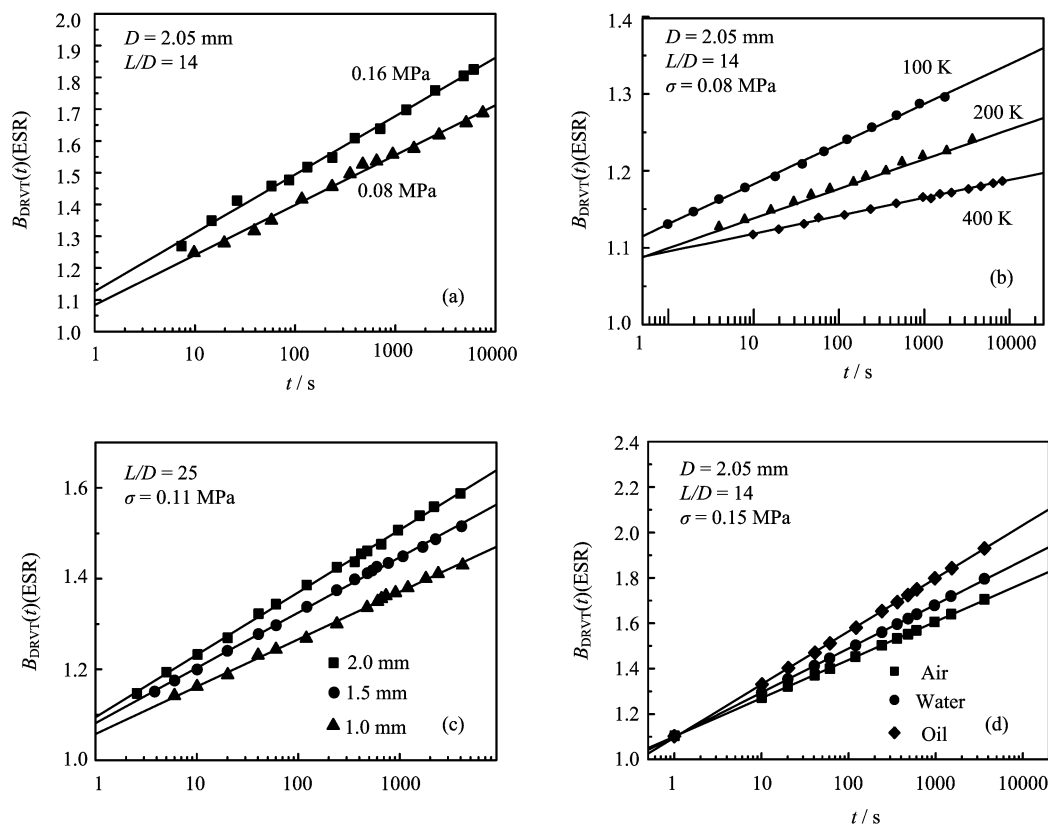


FIG. 4 Dependence of $B_{\text{DRVT}}(t)$ (ESR) on $\lg t$ for the extrude swell of PBD, at 420 K (a); at shear stress of 0.08 MPa, at 420 K (b); three different capillary dies, at 420 K (c); measured by extrusion into oil, water, and air dispersing media, at 420 K (d).

C. Evaluation of swelling ratios from the molecular parameters and the operating variables

Eqs.(58), (59), (62), and (64) show that the theoretical values of B_{IRET} , B_{IRET5} , B_{URVT} , and B_{URVT5} can be directly calculated from the molecular parameters (n' , α , η_0 , G_N^0 , $1-f$ and $1 - \overline{W}_{\dot{\gamma}}$) and the operating variables ($\dot{\gamma}$ and L/D). The evaluated values of B_{IRET} , B_{IRET5} , B_{URVT} , and B_{URVT5} for all samples are given in Fig.3.

D. Comparison of the theoretical values with experimental data

The comparison of the theoretical values B_{IRET} , B_{IRET5} , B_{URVT} , and B_{URVT5} calculated from Eqs.(58), (59), (62), and (64) with corresponding experimental data B_{EXP} are given in Fig.3. They show a series of straight lines passing through the origin. The corresponding inter-correlation coefficients are given in their corresponding figures. The following facts can be seen from the results: The evaluated values of B_{IRET} , B_{IRET5} , B_{URVT} , and B_{URVT5} for all samples are in good agreement with experimental data B_{EXP} , the dynamic theory of die swell in extrudates can be successfully used

to predict the correlation of swelling ratio B in extrudates to their molecular parameters (n' , α , η_0 , G_N^0 , $1-f$ and $1 - \overline{W}_{\dot{\gamma}}$) and the operating variables ($\dot{\gamma}$ and L/D).

The dependencies of η_0 on \overline{M}_W and \overline{M}_e (or concentration) have been deduced from Logarithm Normal Distribution Function (or Lansing-Kraemer Function) [11]. It was found that it may be expressed as:

$$\eta_0 = K (2\overline{M}_e)^{[1-2(2-2M_e/\overline{M}_{nk})]} \overline{M}_W^{-2(2-2M_e/\overline{M}_{nk})} \quad (104)$$

where \overline{M}_e is the number average molecular weight between the entanglement sites, and \overline{M}_{nk} is the number average molecular weight of k th polymeric sample in the total number of polymeric systems. K is a temperature-dependent constant. For a given polymeric system with a given numbers of sample and at a given temperature the \overline{M}_{nk} , \overline{M}_e , and K may be considered as all constants.

When Eq.(89) is used to process the experimental data of PBD shown in Fig.4(b), a series of lines are obtained by plotting $B_{\text{DRVT}}(t)$ against $\lg t$ for PBD with the different molecular weights \overline{M}_W and a given \overline{M}_e (or concentration). These lines are drawn in Fig.4(b). The parameters of D_A and B_A were determined from the slopes and intercepts of these lines with Eq.(89). These values and their inter-correlation coefficients R

are all given in Table III. Then the values of A and $|\lg t_0|$ may be estimated from D_A and B_A using Eqs.(109) and (110). From the expression of A and A_I , the values of $|\lg t_0|$ and the correlation is between the η_0 , \overline{M}_W , and \overline{M}_e in Eq.(104). It is easy to see that the magnitude of D_A may decrease with an increase of \overline{M}_W for the mono disperse polymers ($\overline{M}_W/\overline{M}_n=1$) at 100, 200, and 400 K. The magnitudes of B_A may also decrease with an increase of the \overline{M}_W for the mono disperse polymers ($\overline{M}_W/\overline{M}_n=1$).

Eq.(89) shows that a series of lines are obtained by plotting the $B_{\text{DRV T}}(t)$ against the $\lg t$ for PBD with the different shear stress τ_{12} . These are drawn in Fig.4(a), and the parameters of D_A and B_A were, respectively, determined from the slopes and the intercepts of these lines. These values and their inter-correlation coefficients are all given in Table III. Then the values of A and $|\lg t_0|$ may be estimated from D_A and B_A using Eqs.(109) and (110). Thus, from the expression of A and the value of $|\lg t_0|$, it is easy to see that the magnitude of parameters D_A and B_A all increase with increasing τ_{12} .

Eq.(89) shows that a series of lines are obtained by plotting the logarithm of $B_{\text{DRV T}}(t)$ against the $\lg t$ for the different diameters D . They are drawn in Fig.4(c), and the parameters of D_A and B_A were, respectively, determined from the slopes and the intercepts of these lines. These values and their inter-correlation coefficients are all given in Table III. Then the values of A and $|\lg t_0|$ may be estimated from D_A and B_A using Eqs.(109) and (110). Experimental results show that the magnitude of A is not only related to the molecular parameters and the operational variables, but also controlled by the ratio of flow volume F_V to the free surfaces of the fluids F_S through the relation (Eq.(105)).

$$\frac{F_V}{F_S} = \frac{\pi D^2 L}{4\pi D L} = \frac{\pi D^3 k}{4\pi D^2 k} = \frac{D}{4} \quad \left(\frac{L}{D} = k \right) \quad (105)$$

By replacing the expression of the constant L/D with

TABLE III The molecular parameters of PBD with the different molecular weight and with different operational variables

Figure 4		B_A	D_A	A	$ \lg t_0 $	R
(a)	0.08 MPa	1.0837	0.1572	0.0683	0.3732	0.9969
	0.16 MPa	1.1265	0.1839	0.0798	0.5522	0.9980
(b)	100 K	1.1308	0.0520	0.0226	2.0339	0.9991
	200 K	1.0995	0.0385	0.0167	1.9330	0.9991
	400 K	1.0950	0.0233	0.0101	3.0034	0.9984
(c)	1.0 mm	1.0578	0.1043	0.0453	0.3141	0.9990
	1.5 mm	1.0818	0.1217	0.0529	0.4665	0.9995
	2.0 mm	1.0948	0.1375	0.0597	0.5073	0.9994
(d)	Air	1.1011	0.1687	0.0733	0.4514	0.9999
	Water	1.1005	0.1941	0.0843	0.3891	0.9999
	Oil	1.0966	0.2338	0.1015	0.3062	0.9999

the different F_V/F_S , then the expression of A may be rewritten as

$$A = \frac{(n'\tau_{12})^{1-\overline{W}_\gamma} (1/G_N^0)^{\overline{W}_\gamma/n'} [1 + (D/4)^\alpha]^{\overline{W}_\gamma}}{4 \times 1.050^{1/2} \eta_0^{1+\overline{W}_\gamma(1/n'-1)}} f(0)n_T \quad (106)$$

Thus, from the expression of A and the value of $|\lg t_0|$, it is easily seen that the magnitudes of parameters D_A and B_A all increase with increasing diameter D for $L/D=25$.

Eq.(89) shows that a series of lines are obtained by plotting the logarithm of $B_{\text{DRV T}}(t)$ against $\lg t$. For different dispersing media, these are shown in Fig.4(d). The parameters of D_A and B_A were determined from the slopes and intercepts of these lines. These values and their inter-correlation coefficients are all given in Table III. Then the values of A and $|\lg t_0|$ may be estimated from D_A and B_A using Eqs.(109) and (110). Thus, from the expression of η_0 in Eq.(104) and the values of A and $|\lg t_0|$, it is easy to see that the magnitudes of D_A may increase with an increase of the \overline{M}_e (or with a decrease of the concentration) in the free surface with the different dispersing media (from oil to air). But B_A converged to a constant, which is due to the fact that the value of the product of A and $|\lg t_0|$ is more less than 1.025 constant.

From Eq.(89), we have

$$B_A = 1.025 + 2.303A |\lg t_0| \quad (107)$$

$$D_A = 2.303A \quad (108)$$

From Eqs.(107) and (108) we have

$$A = \frac{D_A}{2.303} \quad (109)$$

$$|\lg t_0| = \frac{B_A - 1.025}{2.303A} \quad (110)$$

Eqs.(109) and (110) show that the values of A and $|\lg t_0|$ can be estimated with D_A and B_A . These estimates are given in Table III. The comparison of the theoretical equation of $B_{\text{DRV T}}(t)$ with experimental data is given in Fig.4. The following facts can be determined by these results: (i) There is a linear correlation between the $B_{\text{DRV T}}(t)$ and the $\lg t$, and a series of lines is obtained by plotting the $B_{\text{DRV T}}(t)$ against the $\lg t$ for PBD with different molecular weights and a given \overline{M}_e (or concentration) at the different operational variables (τ_{12} , L/D , and different dispersing media). (ii) The magnitudes of D_A and B_A decrease with increasing molecular weight \overline{M}_W for the mono-disperse polymers $\overline{M}_W/\overline{M}_n=1$ at 100, 200 and 400 K. (iii) The magnitudes of D_A and B_A increase with increasing shear stress (τ_{12}). (iv) The magnitudes of D_A and B_A increase with increasing diameter D with $L/D=25$. (v) The magnitudes of D_A increase with increasing \overline{M}_e in the different dispersing media (from oil to air), but the magnitudes of B_A approach a constant. The above results show that Eqs.(83) and (89) can be used to predict

the correlation of the delayed extrudate swelling ratio $B_{\text{DRV T}}(t)$ to the molecular parameters (n' , α , η_0 , G_N^0 , f , and $1 - \overline{W}_{\dot{\gamma}}$), the operating variables ($\dot{\gamma}$, τ_{12} , L/D , and different dispersing medium) and the growth time t .

V. CONCLUSION

(i) A new dynamic theory of die swell for the entangled polymeric melts and concentrated solutions in the steady simple shear flow was proposed which is based on the O-W-F constitutive equation and the free recovery by the double transition mechanisms of disentanglement-reentanglement and uncoil-recoil from Poiseuille flow with different ratios L/D of capillary. (ii) A partition function $\psi_1(\dot{\gamma}) \dot{\gamma}/2\eta(\dot{\gamma})$ and two exponential fractions of conformation for the recoil and the viscous heating in the free recovery were defined. (iii) The correlation of the instantaneous $t_r=0$, delayed $t_r=t$, and ultimate $t_r=\infty$ recoverable strain and recoil in the free recovery to the molecular parameters (n' , α , η_0 , G_N^0 , $1-f$ and $1 - \overline{W}_{\dot{\gamma}}$) and the operational variables ($\dot{\gamma}$, τ_{12} , L/D , and t_r) and the dynamics of growth equation on the viscoelastic strain and recoil in the free state were deduced. (iv) After introducing the condition of uniform two dimensional extensions, the definition of $B = \alpha$ and the operational variables into the above correlation expression and growth equations, the correlations of delayed $t_r=t$ and ultimate $t_r=\infty$ extrudate swelling effects to the molecular parameters and the operational variables were determined, and two sets of equations for the growth $t_r=t$ and ultimate $t_r=\infty$ extrudate swelling ratios under the dynamic and equilibrium states were deduced from the dynamic theory of die swell. (v) The first set of equations for the ultimate extrudate swelling ratio under the free and equilibrium states was verified by HDPE experimental data at two temperatures and different operational variables. (vi) The second set of equations on the growth extrudate swelling ratios under the free and dynamic states was verified by PBD experimental data with different molecular weights \overline{M}_W and a give \overline{M}_e using different operational variables. (vii) An excellent agreement between the two theoretical equations on the ultimate and growth extrudate swelling ratios and the experimental results is obtained. The agreements show that the two sets of equations on the ultimate and growth extrudate swell ratios can be used to predict the correlation of the time-dependent and time-independent (or ultimate) extrudate swelling behaviors to the molecular parameters (n' , α , η_0 , G_N^0 , f , and $1 - \overline{W}_{\dot{\gamma}}$) and the operational variables ($\dot{\gamma}$, τ_{12} , L/D , and t_r).

VI. ACKNOWLEDGMENT

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