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Dynamic Theory of Die Swell for Entangled Polymeric Liquids in Tube Extrusion: Correlations of Total and Ultimate Extrudate Swell Effects to Growth Time, Shear Stress and Aspect Ratio Under the Free States

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The dynamic theory of die swell deduced in a previous paper was extensively applied to study the extrudate swelling behaviors of two entangled polymeric liquids (HDPE and PBD) in a simple shear flow at steady shear stress. The mechanism and dynamics for the recoils and the recoveries of viscoelastic strains in the extrudate were investigated under the free recovery and dynamic states. It was found that in the course of recovery the free recoil and the growth of die swell in the extrudate may be divided into two recovery regions (instantaneous and delayed regions) and three growth stages (instantaneous, delayed, and ultimate extrudate swelling stages). The free recoil and the extrudate swelling behaviors may be expressed as a function of shear stress. The correlations of instantaneous, delayed, total and ultimate extrudate swell effects to the molecular parameters and the operational variables in the simple shear flow at steady shear stress were derived from the dynamic theory of die swell. Also, two sets of new universal equations on the total extrudate swelling effect (TESE) and ultimate extrudate swelling effect (UESE) were deduced. The first is the universal equation of the logarithmic correlation between the TESE and the growth time under the free and dynamic states; the second is the universal equation of the logarithmic correlation between the UESE and the operational variables under the free and equilibrium states. The first equation was verified by experimental data of PBD with different molecular weights at different operational variables. The second equation was verified by experimental data of HDPE at two temperatures and different operational variables. An excellent agreement result was obtained. The excellent agreement shows that the two universal equations can be used directly to predict the correlations of the TESE and UESE to the growth time, the molecular parameters, and the operational variables under the dynamic and equilibrium states.

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 extrudate swelling behavior based on bulk flow properties has been a formidable challenge.

There are several studies on the theory of the elastic recoil and the extrudate swell for viscoelastic fluids in the literature [1-9]. The most pertinent for the theory of extrudate swell of the polymeric melts and the entangled polymeric liquids would seem to be that of Tanner [4] and of Song [7-9]. The former is based on the KBKZ constitutive equation and the free recovery from Poiseuille flow with the aspect ratio of length L to diameter D approaching to ∞ . The latter is based on the O-W-F constitutive equation and the free recovery by the double mechanisms [10] of reentanglement-disentanglement transition (RE-DT) and recoil-uncoil

transition (RC-UCT) from the Poiseuille flow with the different ratio of L/D . It was found that these ultimate extrudate swell behaviors may be expressed by the following relations:

For the expression of ultimate extrudate swell ratio B by Tanner [4]

$$B = \frac{D_f}{D_0} = 0.13 + \left[1 + \frac{1}{8} \left(\frac{N_1}{\tau_{12}} \right)_W^2 \right]^{1/6} \quad (1)$$

For the expression of ultimate extrudate swell ratio $B_{URVT}(\infty)$ by Song [7,8]

$$B_{URVT}(\infty) = \left[\frac{1}{8} \left(\frac{N_1}{\tau_{12}} \right)_W + \frac{5.098}{4} \right]^{1/2} \quad (2)$$

$$B_{URVT}(\infty) = \left\{ \frac{1}{4} \left[\frac{n' (\eta_0/G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}\dot{\gamma}} + \frac{5.098}{4} \right\}^{1/2} \quad (3)$$

where N_1 and τ_{12} are the first normal difference and the shear stress. η_0 represents the shear viscosity at the

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zero shear rate, $G_N^0 = \rho RT / \bar{M}_e$, ρ is the density of polymeric melts, and \bar{M}_e is the molecular weight between entanglement sites. n' and α are, respectively, the average constrained dimensional numbers of terminal and loop constituent chains. $1 - \bar{W}_\gamma$ is the fraction of the recoverable conformation on the entangled polymeric chain (or at entangled state) and $\dot{\gamma}$ is the shear rate. $B_{URVT}(\infty)$ represents the ultimate extrudate swelling ratio at the recoverable time ($t_r = \infty$).

It is apparent that Eq.(3) can be used directly to predict the correlation of the ultimate extrudate swelling behaviors to the molecular parameters and n' , α , η_0 , G_N^0 , $1 - \bar{W}_\gamma$, and the operational variables ($\dot{\gamma}$ and L/D).

It is evident in Eqs.(1) to (3) that the time-dependent nature of the extrudate swelling behavior of viscoelastic fluids is not considered. The experimental study on the correlation of the true viscoelastic behavior of extrudate swell to the primary structure of polymeric chain (\bar{M}_n , \bar{M}_w/\bar{M}_n , and \bar{M}_e) and the operational processes condition (τ_{12} and L/D) have been, respectively, carried out by Koopmans [11] and Wang [12], but the theoretical research on the theoretical framework for this correlation still has been never reported.

Recently, in a previous paper [9] a new dynamic theory of die swell for the entangled polymeric liquids in the tube extrusion under free state was proposed and a new equation on the delayed extrudate swelling ratio (DESR and $B_{DRVT}(t)$) was derived from the dynamic theory. It may be expressed as

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

where n_T is the total numbers of the moles for the disentanglement polymer chains per unit volume taking part in the reorganization of entangled constituent chains over the time interval t , μ_0 is the reformation rate constant for the entangled constituent chain on each disentangled polymeric chain, $f(0)$ is a critical fraction of gauche-form conformation to be reorganized for the entanglement sites on each disentangled polymeric chain at the front of the recoverable time t_0 and t are the initial and growth time.

It is easy to see that Eq.(4) can be successfully used to predict the correlation of DESR and $B_{DRVT}(t)$ to the molecular parameters, the growth times, and the operational variables under steady shear stress.

Experimental results show that [8,13] two type functions are usually used to characterize the total or ultimate extrudate swelling effect and swelling ratio for entangled polymeric liquids in the steady shear flow. One is the ultimate extrudate swelling effect and swelling ratio as the function of shear rate shown in Eq.(3); the other one is the total or ultimate extrudate swelling effect and swelling ratio as the function of shear stress

[12,13]. But the theoretical expression for the correlation of the total and ultimate extrudate swelling effects and swelling ratios to the growth time, the molecular parameters and the operational variables as a function of τ_{12} and L/D has never been reported. Therefore, in this paper the dynamic theory of die swell was extensively applied to study the extrudate swell behaviors of entangled polymeric liquids in the tube extrusion under the steady state of shear stress. Also, the correlation of the total and ultimate extrudate swelling effects to the growth time t_r , shear rate τ_{12} and aspect ratio L/D under the free and dynamic state was deduced from the dynamic theory of die swell.

II. CORRELATION OF TOTAL AND ULTIMATE EXTRUDATE SWELLING EFFECTS TO THE GROWTH TIME, SHEAR STRESS AND ASPECT RATIO UNDER THE FREE AND DYNAMIC STATES

A. Mechanism and dynamics for the instantaneous, delayed and ultimate recoils and recoveries of recoverable viscoelastic strains in the extrudate

Figures 1 and 2 illustrate the phenomenon of die swell resulting from the instantaneous, delayed and ultimate

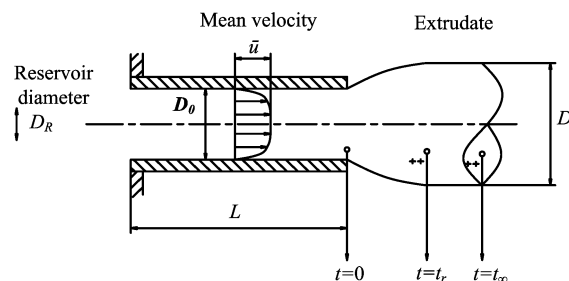


FIG. 1 Sketch of extrudate swell with viscoelastic recovery (Reproduced with permission from Ref.[4]. Copyright 1970 Journal of Polymer Science).

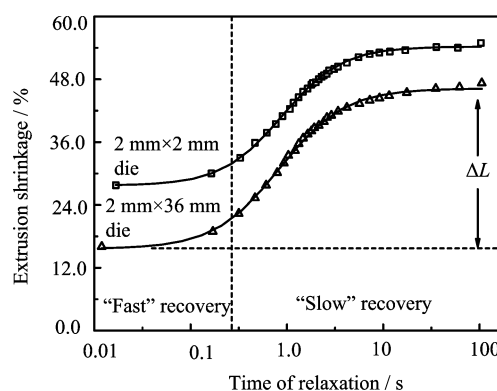


FIG. 2 Post-extrusion relaxation curves for SBR-1500 containing 50 phr N330 black extruded at 360 s^{-1} shear rate (Reproduced with permission from Ref.[10]. Copyright 2004 Macromolecules).

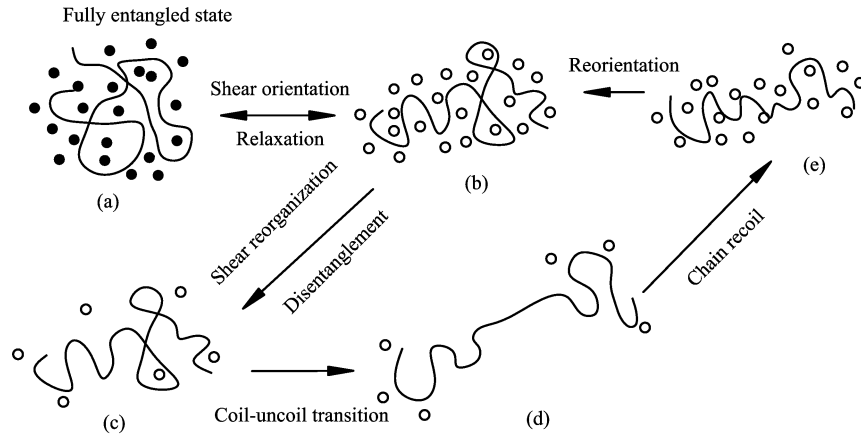


FIG. 3 Sketch of steps leading to entanglement-disentanglement and coil-uncoil under constant-stress shear as well as chain recoil the five ((a) to (e)) and relaxation from the disentangled state after turning off the applied shear stress (Reproduced with permission from Ref.[19]. Copyright 1979 Rubber Chemistry and Technology).

mate recoils and the recoveries of recoverable viscoelastic strains in the extrudate to a larger diameter D_f than the tube diameter D_0 as it emerges from the tube. From the molecular and dynamic theory of die swell in previous papers [8,9] combined with Figs.1 and 2, it is easy to determine that in the course of the recovery process the free recoil and the growth of die swell in the radial direction for the extrudate may be divided into the following different regions and stages: (i) Instantaneous elastic recovery region and stage at $t_r=0$. In the region and stage the correlation between the instantaneous recoverable elastic strain and the instantaneous elastic recoil may be expressed as

$$(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)_{t_r=0} = \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{W,S.F} \right]^{\tau_{12}} \cdot (1 - f_e) \quad (5)$$

(ii) Delayed viscoelastic recovery region and stage at $t_r=t$. In the region and stage the correlation between the delayed recoverable strain and the delayed recoil may be expressed as

$$\ln \left[\frac{1}{3} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2) \right] (t) = \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{W,S.F} \right]^{\tau_{12}} f(t) \quad (6)$$

(iii) Ultimate elastic and viscoelastic recovery stage at $t_r=\infty$. In the stage the correlation between the ultimate (or total) recoverable strains and the ultimate (or total) recoil may be expressed as

$$(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)_{t=0} + \ln \left[\frac{1}{3} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2) \right]_{t=\infty} = \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{W,S.F} \right]^{\tau_{12}} (\infty) \quad (7)$$

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

$(1 - f_e)$ is a time-independent fraction of trans-form conformation in the constituent chains to be taken part in the rearrangement of the population conformation at the beginning of recoverable time ($t_r=0$). $f(t)$ is the fraction of gauche-form conformation on the disentangled polymeric chains which can be reorganized for the entanglement sites at t_r .

In this course of molecular relaxation there are two physical quantities to be determined. One is the extrudate swell ratio B in the radial direction as given in Fig.1, which is defined as $B=D_f/D_0$; the other one is the extrusion shrinkage L in the axial direction as given in Fig.2 [19], which is defined as the percent decrease in the extrudate length by $L=(1-l/l_0) \times 100\%$, where l and l_0 are, respectively, the theoretical (without the change in volume) and actual lengths of the extrudate. For incompressible liquids there is a correlation between B and L . Therefore, only one physical quantity (B or L) is the independent variable.

Figure 3 illustrates the main physical features [10] for the chain disentanglement transition under shear and the chain recoil and relaxation leading to the chain reentanglement upon withdrawal of shear. It depicts the five different stages during the RE-DT at a constant stress.

From Fig.3, the structural model of transit entanglement network and the multiple-reptation mechanism of polymeric chains by the dynamic reorganization of entanglement sites [7,8]. It is easy to distinguish the two types of molecular relaxation process occurring in the above two different regions. 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 a slow process and are taken to be delayed; (ii) the process of the rearrangement for the population conformation from trans-form $(1-f)$ to f on the ex-

tending segment of constituent chains, which is a fast process and is taken to be instantaneous. The two types of the molecular process which at very different rates of relaxation can be characterized by the function of $\left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}}$ and the fractions of gauche- and transform conformations on the entangled and disentangled polymeric chains. The correlations between the ultimately free recoil and the ultimate recoverable strain, between the instantaneously free recoil and the instantaneous recoverable strain, and between the delayed free recoil and the delayed recoverable strain in the steady shear stress and recoverable time has been deduced in the previous papers [7,8]. It was found that they may be characterized by the following relations: (i) The instantaneously recoverable strain and instantaneous elastic recoil in the steady shear stress τ_{12} and the instantaneously recovery time $t=0$

$$\begin{aligned} [S_{IRET}(0)]_{S.F}^{\tau_{12}} &= [S_{URVT}(\infty)]_{S.F}^{\tau_{12}}(1 - f_e) \\ &= \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}}(1 - f_e) \\ &= (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)_{t_r=0} \quad (8) \end{aligned}$$

(ii) The delayed recoverable viscoelastic strain and delayed viscoelastic recoil in τ_{12} and $t_r=t$

$$\begin{aligned} [S_{DRVT}(t)]_{S.F}^{\tau_{12}} &= [S_{URVT}(\infty)]_{S.F}^{\tau_{12}}f(t) \\ &= \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}}f(t) \\ &= \left\{\ln\left[\frac{1}{3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)\right](t)\right\} \quad (9) \end{aligned}$$

When $f_e=f(0)n_T\mu_0\ln(t_\infty/t_0)$, it is the fraction of gauche-form conformation on each disentangled polymeric chain to be taken part in the reorganization of entanglement sites at the recoverable time which approached to the infinite ($t_r=\infty$), its value is a limited constant. t_0 is the extrapolated initial time. Therefore, in the course of recovery there are a series of rearrangements of population conformation and the reentanglement of constituent chain to occur until they approach to the equilibrium state. (iii) The ultimately recoverable viscoelastic strain and ultimately viscoelastic recoil in τ_{12} and $t_r=\infty$.

This may be expressed as the summation of its components [7,8] at $t_r=\infty$. Thus, we have

$$\begin{aligned} [S_{URVT}(\infty)]_{S.F}^{\tau_{12}} &= [S_{IRET}(0)]_{S.F}^{\tau_{12}} + [S_{DRVT}(\infty)]_{S.F}^{\tau_{12}} \\ &= \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}} [(1 - f_e) + f_e] \\ &= \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}} (\infty) \\ &= [2(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) - 5.098]_{t_r=\infty} \quad (10) \end{aligned}$$

From the above sections and Figs.1 to 3, 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 conformation 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, during the recoil and extrudate swelling proceed the rate of change in the quantities of delayed recoil and the delayed recoverable viscoelastic strains is not only determined by the rate of change n_T/t in the total mole numbers n_T of disentangled polymeric chains per unit volume to be taken part in the reorganization of entangled constituent chain over the time interval t , but also controlled by the reformation rate constant of the reentangled constituent chains on the each disentangled polymeric chain μ_0 . Therefore, their reformation rate may be characterized by the following equations:

$$\frac{d}{dt} \left\{ \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}} f(t) \right\} = \mu_0 \frac{n_T}{t} \quad (11)$$

$$\frac{d}{dt} \left\{ \ln \left[\frac{1}{3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) \right] (t) \right\} = \mu_0 \frac{n_T}{t} \quad (12)$$

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

$$\begin{aligned} \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}} f(t) &= \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}} \\ &\cdot f(0)n_T\mu_0\ln\frac{t}{t_0} \quad (13) \end{aligned}$$

$$\begin{aligned} \ln \left\{ \left[\frac{1}{3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)\right] (t) \right\} &= \ln \left[\frac{1}{3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) \right] \\ &\cdot f(0)n_T\mu_0\ln\frac{t}{t_0} \quad (14) \end{aligned}$$

By comparison with Eqs.(13) and (14), it is easy to obtain the following equation:

$$\begin{aligned} \ln \left\{ \left[\frac{1}{3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)\right] (t) \right\} &= \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}} f(t) \\ &= \left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}} \\ &\cdot f(0)n_T\mu_0\ln\frac{t}{t_0} \quad (15) \end{aligned}$$

where μ_0 may be expressed as [9]

$$\begin{aligned} \mu_0 &= \frac{1}{\tau_0} = \left(\frac{G_N^0}{\eta_0}\right)^{1/n'} (1 + D_e^\alpha) \\ &= \left(\frac{G_N^0}{\eta_0}\right)^{1/n'} \left[1 + \left(\frac{\eta_0\dot{\gamma}}{G_N^0}\right)^\alpha\right] \quad (16) \end{aligned}$$

$$\begin{aligned}\mu_0 &= \frac{1}{\tau_0} = \left(\frac{G_N^0}{\eta_0}\right)^{1/n'} (1 + D_e^\alpha) \\ &= \left(\frac{G_N^0}{\eta_0}\right)^{1/n'} \left[1 + \left(\frac{\tau_{12}}{G_N^0}\right)^\alpha\right]\end{aligned}\quad (17)$$

$$\begin{aligned}\mu_0 &= \frac{1}{\tau_0} = \left(\frac{G_N^0}{\eta_0}\right)^{1/n'} (1 + D_e^\alpha) \\ &= \left(\frac{G_N^0}{\eta_0}\right)^{1/n'} \left[1 + \left(\frac{L}{D}\right)^\alpha\right]\end{aligned}\quad (18)$$

Eqs.(16), (17), and (18) can be successfully used to predict the correlations of $\mu_0=1/\tau_0$ to the molecular parameters and the operational variables.

B. Correlation of instantaneous, delayed and ultimate extrudate swelling effects to the molecular parameters and the operational variables

The correlation of $\left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}}$ to the molecular parameters (n' , α , η_0 , G_N^0 , and $1 - \bar{W}_\dot{\gamma}$) and the operational variables (τ_{12} and L/D) have been deduced in previous work [7,8]. It was found that it may be expressed as

$$\left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\dot{\gamma}} = \left[\frac{n'(\eta_0/G_N^0)^{1/n'}\dot{\gamma}}{1 + (L/D)^\alpha}\right]^{1-\bar{W}_\dot{\gamma}}\quad (19)$$

After introducing the relation $\tau_{12}=\eta_0 \cdot \dot{\gamma}$, we have

$$\left[\frac{1}{2}\left(\frac{N_1}{\tau_{12}}\right)_W\right]_{S.F}^{\tau_{12}} = \left[\frac{n'(\eta_0/G_N^0)^{1/n'}(\tau_{12}/\eta_0)}{1 + (L/D)^\alpha}\right]^{1-\bar{W}_\dot{\gamma}}\quad (20)$$

The state of deformation for swelling ratio B of extrudates may be considered as the uniform two-dimensional extension [14], in this type of strain the sample is stretched by equal amounts in two directions at right angles. If the stretch ratio is α , there are $\alpha_x=\alpha_y=\alpha$; $\alpha_z=\alpha^{-2}$. First introducing the above relations into Eqs.(8)-(10), then replacing the stretch ratio by the swelling ratio ($B=\alpha$) and combining these equations with Eqs.(15) and (20), we obtain the correlation of instantaneous, delayed, total and ultimate extrudate swelling effects to the molecular parameters and the operational variables under the free state and recoverable (or growth) time.

These correlations may be expressed by the following equations: (i) The instantaneous extrudate swelling effect (IESE) as a function of τ_{12} at the recoverable (or growth) time ($t_r=0$). Eq.(21) shows that the instantaneous extrudate swelling effect results from the rearrangement of the population conformation of segments

in the constituent chains.

$$\begin{aligned}2B_{\text{IRET}}^2(0) + \frac{1}{B_{\text{IRET}}^4(0)} - 3.0 \\ = \left[\frac{n'(1/G_N^0)^{1/n'}\eta_0^{1/n'-1}\tau_{12}}{1 + (L/D)^\alpha}\right]^{1-\bar{W}_\dot{\gamma}} \\ \cdot \left[1 - f(0)n_T\mu_0 \ln \frac{t_\infty}{t_0}\right] \\ = \left[\frac{n'(1/G_N^0)^{1/n'}\eta_0^{1/n'-1}\tau_{12}}{1 + (L/D)^\alpha}\right]^{1-\bar{W}_\dot{\gamma}} (1 - f_e)\end{aligned}\quad (21)$$

(ii) The delayed extrudate swelling effect (DESE) as a function of τ_{12} at $t_r=t$

$$\begin{aligned}2B_{\text{DRV T}}^2(t) + \frac{1}{B_{\text{DRV T}}^4(t)} - 2.098 \\ = \left[\frac{n'(1/G_N^0)^{1/n'}\eta_0^{1/n'-1}\tau_{12}}{1 + (L/D)^\alpha}\right]^{1-\bar{W}_\dot{\gamma}} \\ \cdot f(0)n_T\mu_0 \ln \frac{t}{t_0}\end{aligned}\quad (22)$$

Eq.(22) 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 extrudate swelling effect (TESE) as a function of τ_{12} at $t_r=t$

$$\begin{aligned}4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 \\ = \left[2B_{\text{IRET}}^2(0) + \frac{1}{B_{\text{IRET}}^4(0)} - 3.0\right] \\ + \left[2B_{\text{DRV T}}^2(t) + \frac{1}{B_{\text{DRV T}}^4(t)} - 2.098\right] \\ = \left[\frac{n'(1/G_N^0)^{1/n'}\eta_0^{1/n'-1}\tau_{12}}{1 + (L/D)^\alpha}\right]^{1-\bar{W}_\dot{\gamma}} \\ \cdot \left\{\left[1 - f(0)n_T\mu_0 \ln \left(\frac{t_\infty}{t_0}\right)\right] \right. \\ \left. + f(0)n_T\mu_0 \ln \frac{t}{t_0}\right\} \\ = \left[\frac{n'(1/G_N^0)^{1/n'}\eta_0^{1/n'-1}\tau_{12}}{1 + (L/D)^\alpha}\right]^{1-\bar{W}_\dot{\gamma}} \\ \cdot \left[(1 - f_e) + f(0)n_T\mu_0 \ln \frac{t}{t_0}\right]\end{aligned}\quad (23)$$

where $f_e=f(0)n_T\mu_0 \ln(t_\infty/t_0)$. It is a limited fraction of gauche-form conformation at t_r that approach to infinity $t_r=\infty$. When $t_r=t=\infty$, then Eq.(23) reduced to the ultimate extrudate swelling effect. (iv) The ultimate extrudate swelling effect (UESE) as a function of

shear stress at $t_r=\infty$

$$\begin{aligned}
 & 4B_{\text{URVT}}^2(\infty) + \frac{2}{B_{\text{URVT}}^4(\infty)} - 5.098 \\
 &= \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} [(1-f_e) + f_e] \\
 &= \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \quad (24)
 \end{aligned}$$

When $1-\bar{W}_\gamma=1/2$, then Eqs.(23) and (24) reduce to the following equations:

$$\begin{aligned}
 & 4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 \\
 &= \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1/2} \\
 &\cdot \left\{ \left[1 - f(0)n_T\mu_0 \ln \frac{t_\infty}{t_0} \right] \right. \\
 &\quad \left. + f(0)n_T\mu_0 \ln \frac{t}{t_0} \right\} \quad (25)
 \end{aligned}$$

$$\begin{aligned}
 & 4B_{\text{URVT}}^2(\infty) + \frac{2}{B_{\text{URVT}}^4(\infty)} - 5.098 \\
 &= \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1/2} \quad (26)
 \end{aligned}$$

Eqs.(25) and (26) show that these equations are a universal equation for characterizing the total and ultimate extrudate swelling effects in the extrudate at the isoviscoelastic state $1-\bar{W}_\gamma=1/2$ under the dynamic and equilibrium conditions.

C. Correlation of total extrudate swelling effect to the molecular parameters, the growth time and the operational variables for entangled polymeric liquids in the steady shear flow

From Eq.(23), it is easy to know that the TESE may be rewritten as

$$\begin{aligned}
 & 4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 \\
 &= \left[\frac{n'(1/G_N^0)^{1/n'} \eta_0^{1/n'-1} \tau_{12}}{1 + (L/D)^\alpha} \right]^{1-\bar{W}_\gamma} \\
 &\cdot (1-f_e) \left[1 + \frac{2.303f(0)n_T\mu_0}{1-f_e} \lg \frac{t}{t_0} \right] \quad (27)
 \end{aligned}$$

where $1-f_e=1-2.303f(0)n_T\mu_0 \lg(t/t_0)$ is a limited constant. Taking the logarithms on both sides, we have

$$\begin{aligned}
 & \lg \left[4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 \right] \\
 &= \lg \left\{ \left[\frac{n'(n_0/G_N^0)^{1/n'} \tau_{12}}{[1 + (L/D)^\alpha] \eta_0} \right]^{1-\bar{W}_\gamma} (1-f_e) \right\} \\
 &\quad + \lg \left[1 + \frac{2.303f(0)n_T\mu_0}{1-f_e} \lg \frac{t}{t_0} \right] \quad (28)
 \end{aligned}$$

$\lg(1+x) \doteq x$, Eq.(28) may be approximately expressed as

$$\begin{aligned}
 & \lg \left[4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 \right] \\
 &= \lg \left\{ \left[\frac{n'(\eta_0/G_N^0)^{1/n'} \tau_{12}}{[1 + (L/D)^\alpha] \eta_0} \right]^{1-\bar{W}_\gamma} (1-f_e) \right\} \\
 &\quad + \frac{2.303f(0)n_T\mu_0}{1-f_e} \lg \frac{t}{t_0} \quad (29)
 \end{aligned}$$

Because the value of t_0 is almost less than unity [12], therefore the above equation may be rewritten as

$$\begin{aligned}
 & \lg \left[4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 \right] \\
 &= \lg \left\{ \left[\frac{n'(\eta_0/G_N^0)^{1/n'} \tau_{12}}{[1 + (L/D)^\alpha] \eta_0} \right]^{1-\bar{W}_\gamma} (1-f_e) \right\} \\
 &\quad + \left[\frac{2.303f(0)n_T\mu_0}{1-f_e} \right] |\lg t_0| \\
 &\quad + \left[\frac{2.303f(0)n_T\mu_0}{1-f_e} \right] \lg t \\
 &= A_0 + B_0 \lg t \quad (30)
 \end{aligned}$$

where $|\lg t_0|$ represents the absolute value to be taken,

$$\begin{aligned}
 A_0 &= \lg \left\{ \left[\frac{n'(\eta_0/G_N^0)^{1/n'} \tau_{12}}{[1 + (L/D)^\alpha] \eta_0} \right]^{1-\bar{W}_\gamma} (1-f_e) \right\} \\
 &\quad + \left[\frac{2.303f(0)n_T\mu_0}{1-f_e} \right] |\lg t_0| \quad (31)
 \end{aligned}$$

$$B_0 = \frac{2.303f(0)n_T\mu_0}{1-f_e} \quad (32)$$

Then Eq.(31) may be rewritten as the following expression:

$$\begin{aligned}
 A_0 &= \lg \left\{ \left[\frac{n'(\eta_0/G_N^0)^{1/n'} \tau_{12}}{[1 + (L/D)^\alpha] \eta_0} \right]^{1-\bar{W}_\gamma} (1-f_e) \right\} + B_0 |\lg t_0| \\
 &= A_{10} + B_0 |\lg t_0| \quad (33)
 \end{aligned}$$

$$A_{10} = \lg \left\{ \left[\frac{n'(\eta_0/G_N^0)^{1/n'} \tau_{12}}{[1 + (L/D)^\alpha] \eta_0} \right]^{1-\bar{W}_\gamma} (1-f_e) \right\} \quad (34)$$

Eq.(29) is a universal equation of the logarithmic correlation between the total extrudate swelling effect and the growth time. It can be used to predict the correlation of total extrudate swelling effect to the growth time for the different polymeric liquids in the steady shear flows at the different operational variables (τ_{12} and L/D). A_{10} represents the logarithms of the magnitudes for the instantaneous extrudate swelling effect at $t_r=0$, B_0 represents the rate of growth for the delayed extrudate swelling effect and $A_0=A_{10} + B_0|\lg t_0|$.

The parameters of B_0 and A_0 can be determined from the slope and intercept of the line by plotting $\lg(\text{TESE})$ ($\lg[4B_{\text{URVT}}^2(t) + 2/B_{\text{URVT}}^4(t) - 5.098]$) against $\lg t$. Eq.(30) shows that there are linear relation between the $\lg(\text{TESE})$ and $\lg t$, a series of lines may be obtained by plotting $\lg(\text{TESE})$ against $\lg t$ for the different polymeric fluids under the different operational variables (τ_{12} and L/D). Then a set of parameters of B_0 and A_0 may be determined from the slopes and intercepts of the lines.

The parameters of A_{10} for the different polymeric fluids at the different operational variables can be directly calculated from the following relation with a given t_0

$$A_{10} = A_0 - B_0|\lg t_0| \quad (35)$$

The expressions of the parameters for B_0 and A_{10} can be obtained from Eqs.(32) and (34). According to Eqs.(16), (17), and (18), they may be, respectively, expressed as

$$B_{0(\tau)} = \frac{2.303f(0)n_T\mu_0}{1-f_e} = \frac{2.303f(0)n_T}{1-f_e} \left(\frac{G_N^0}{\eta_0}\right)^{1/n'} \left[1 + \left(\frac{\tau_{12}}{G_N^0}\right)^\alpha\right] \quad (36)$$

$$B_{0(L/D)} = \frac{2.303f(0)n_T}{1-f_e} \left(\frac{G_N^0}{\eta_0}\right)^{1/n'} \left[1 + \left(\frac{L}{D}\right)^\alpha\right] \quad (37)$$

$$A_{10} = \lg \left\{ \left[\frac{n' (1/G_N^0)^{1/n'} \tau_{12}}{[1 + (L/D)^\alpha] \eta_0^{1-1/n'}} \right]^{1-\bar{W}_{\dot{\gamma}}} (1-f_e) \right\} \quad (38)$$

Eqs.(36), (37), and (38) show that there are the correlations of the $B_{0(\tau)}$, $B_{0(L/D)}$, and A_{10} parameters to the molecular parameters (n' , α , η_0 , G_N^0 , $1-\bar{W}_{\dot{\gamma}}$, $1-f_e$, $f(0)$, and n_T) and the operational variables (τ_{12} and L/D).

The dependences η_0 on the \bar{M}_W and \bar{M}_e (or concentration) have been deduced from Logarithm Normal Distribution Function (or Lansing-Kraemer Function) in a previous work [9]. It was found that it can be expressed as

$$\eta_0 = K \left(\frac{1}{2\bar{M}_e} \right)^{2(2-2\bar{M}_e/\bar{M}_{nk})-1} \bar{M}_W^{2(2-2\bar{M}_e/\bar{M}_{nk})} \quad (39)$$

where \bar{M}_e is the number average molecular weight between the entanglement sites, and \bar{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 \bar{M}_{nk} , \bar{M}_e , and K may all be considered as constants.

D. The universal equation on the logarithmic correlation between the UESE and the operational variables for a given polymeric liquid

Taking the logarithms on both sides of Eq.(24), we have

$$\begin{aligned} & \lg \left[4B_{\text{URVT}}^2(\infty) + \frac{2}{B_{\text{URVT}}^4(\infty)} - 5.098 \right] \\ &= (1 - \bar{W}_{\dot{\gamma}}) \lg \left[\frac{n' (\eta_0/G_N^0)^{1/n'}}{\eta_0} \right] \\ &+ (1 - \bar{W}_{\dot{\gamma}}) \lg \left\{ \frac{\tau_{12}}{[1 + (L/D)^\alpha]} \right\} \quad (40) \end{aligned}$$

Letting $y = \lg \left[4B_{\text{URVT}}^2(\infty) + \frac{2}{B_{\text{URVT}}^4(\infty)} - 5.098 \right]$, then Eq.(40) may be rewritten as

$$\begin{aligned} y &= (1 - \bar{W}_{\dot{\gamma}}) \lg \left[\frac{n' (\eta_0/G_N^0)^{1/n'}}{\eta_0} \right] \\ &+ (1 - \bar{W}_{\dot{\gamma}}) \lg \left[\frac{\tau_{12}}{1 + (L/D)^\alpha} \right] \\ &= B + A_S \lg \left[\frac{\tau_{12}}{1 + (L/D)^\alpha} \right] \quad (41) \end{aligned}$$

$$A_S = (1 - \bar{W}_{\dot{\gamma}})_S \quad (42)$$

$$B = (1 - \bar{W}_{\dot{\gamma}}) \lg \left[\frac{n' (\eta_0/G_N^0)^{1/n'}}{\eta_0} \right] \quad (43)$$

Eq.(41) shows that there is a linear relation between y and $\lg \left[\frac{\tau_{12}}{1 + (L/D)^\alpha} \right]$, thus, a line can be obtained by plotting y against $\lg \left[\frac{\tau_{12}}{1 + (L/D)^\alpha} \right]$.

Eq.(41) shows that the parameters of A_S and B averaging over the whole pairs between τ_{12} and L/D can be determined from the slope and intercept of the lines by plotting y against $\lg \left[\frac{\tau_{12}}{1 + (L/D)^\alpha} \right]$.

For a given polymeric liquid and a given set of capillary L/D the values of n' , α , η_0 , G_N^0 , and L/D are all constants. By taking the logarithms on both sides of

Eq.(24), then it may be rewritten in the following form:

$$\begin{aligned} & \lg \left[4B_{\text{URVT}}^2(\infty) + \frac{2}{B_{\text{URVT}}^4(\infty)} - 5.098 \right] \\ &= (1 - \overline{W}_{\dot{\gamma}})_{\tau_{12}} \lg \left\{ \frac{n'(\eta_0/G_N^0)^{1/n'}}{[1 + (L/D)^\alpha]\eta_0} \right\} \\ & \quad + (1 - \overline{W}_{\dot{\gamma}})_{\tau_{12}} \lg \tau_{12} \end{aligned} \quad (44)$$

Let $y = \lg \left[4B_{\text{URVT}}^2(\infty) + \frac{2}{B_{\text{URVT}}^4(\infty)} - 5.098 \right]$. Then Eq.(44) may be rewritten as

$$\begin{aligned} y &= (1 - \overline{W}_{\dot{\gamma}})_{\tau_{12}} \lg \left\{ \frac{n'(\eta_0/G_N^0)^{1/n'}}{[1 + (L/D)^\alpha]\eta_0} \right\} \\ & \quad + (1 - \overline{W}_{\dot{\gamma}})_{\tau_{12}} \lg \tau_{12} \\ &= B_1 + A_1 \lg \tau_{12} \end{aligned} \quad (45)$$

$$A_1 = (1 - \overline{W}_{\dot{\gamma}})_{\tau_{12}} \quad (46)$$

$$B_1 = (1 - \overline{W}_{\dot{\gamma}})_{\tau_{12}} \lg \left\{ \frac{n'(\eta_0/G_N^0)^{1/n'}}{[1 + (L/D)^\alpha]\eta_0} \right\} \quad (47)$$

Eq.(45) shows that there is a linear relation between y and $\lg \tau_{12}$.

For a given polymeric liquid and a given τ_{12} , the values of n' , α , η_0 , G_N^0 , and τ_{12} are all constants. By taking the logarithms on both sides of Eq.(24), then it may be rewritten in the following form:

$$\begin{aligned} & \lg \left[4B_{\text{URVT}}^2(\infty) + \frac{2}{B_{\text{URVT}}^4(\infty)} - 5.098 \right] \\ &= (1 - \overline{W}_{\dot{\gamma}})_{(L/D)} \lg \left[\frac{n'(\eta_0/G_N^0)^{1/n'} \tau_{12}}{\eta_0} \right] \\ & \quad + (1 - \overline{W}_{\dot{\gamma}})_{(L/D)} \lg \left[\frac{1}{1 + (L/D)^\alpha} \right] \end{aligned} \quad (48)$$

Letting $y = \lg \left[4B_{\text{URVT}}^2(\infty) + \frac{2}{B_{\text{URVT}}^4(\infty)} - 5.098 \right]$, Eq.(48) may be rewritten as

$$y = B_2 + A_2 \lg \left[\frac{1}{1 + (L/D)^\alpha} \right] \quad (49)$$

$$A_2 = (1 - \overline{W}_{\dot{\gamma}})_{(L/D)} \quad (50)$$

$$B_2 = (1 - \overline{W}_{\dot{\gamma}})_{(L/D)} \lg \left[\frac{n'(\eta_0/G_N^0)^{1/n'} \tau_{12}}{\eta_0} \right] \quad (51)$$

Eq.(49) shows that there is a linear relation between y and $\lg \left[\frac{1}{1 + (L/D)^\alpha} \right]$.

From the intercept of the lines by plotting y against

$\lg \tau_{12}$ with Eq.(45), we have

$$\begin{aligned} \frac{B_1}{(1 - \overline{W}_{\dot{\gamma}})_{\tau_{12}}} &= \lg \left[\frac{n'(\eta_0/G_N^0)^{1/n'}}{[1 + (L/D)^\alpha]\eta_0} \right] = \frac{B_1}{A_1} \\ &= \lg \left[\frac{n'(1/G_N^0)^{1/n'}}{\eta_0^{1-1/n'}} \right] \\ & \quad + \lg \left[\frac{1}{1 + (L/D)^\alpha} \right] \end{aligned} \quad (52)$$

Eq.(52) shows that this is a linear relation between B_1/A_1 and $\lg \left[\frac{1}{1 + (L/D)^\alpha} \right]$.

From the intercepts of the lines by plotting y against $\lg \left[\frac{1}{1 + (L/D)^\alpha} \right]$ with Eq.(48), we have

$$\begin{aligned} \frac{B_2}{(1 - \overline{W}_{\dot{\gamma}})_{L/D}} &= \lg \left[\frac{n'(\eta_0/G_N^0)^{1/n'} \tau_{12}}{\eta_0} \right] = \frac{B_2}{A_2} \\ &= \lg \left[\frac{n'(1/G_N^0)^{1/n'}}{\eta_0^{1-1/n'}} \right] + \lg \tau_{12} \end{aligned} \quad (53)$$

Eq.(53) shows that this is a linear relation between B_2/A_2 and the $\lg \tau_{12}$.

III. COMPARISON OF THEORETICAL EQUATIONS WITH EXPERIMENTS

A. Experimental results

The dependence of $\eta(\dot{\gamma})$ and $\psi_1(\dot{\gamma})$ on the shear rate $\dot{\gamma}$ [15] and the dependence of ultimate extrudate swelling ratio B on $\dot{\gamma}$, τ_{12} , and L/D for the linear polyethylene (HDPE) under the condition of flow stability have been studied by Chan and others [16-18]. These results are given in Fig.4.

The dependence of total extrudate swelling ratio $B_{\text{URVT}}(t) = D'_f(t)/D_0$ on the function of for the $\lg(t/t_0)$ linear polybutadiene (PBD) with different molecular weights \overline{M}_W and a given \overline{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 [12]. These results are also given in Fig.5. Figure 1 (given in reference [12]) shows that the value of the extrapolated initial time t_0 is larger than zero ($1 > t_0 > 0$) [12], thus we have $D(t_0) > D_0$. For distinguishing the contributions of $B_{\text{URVT}}(t)$ and $B_{\text{DRVT}}(t)$ to their extrudate swelling effect (TESE and DESE) the following two different extrudate swelling ratios (TESR and DESR) must be defined: $B_{\text{URVT}}(t) = D'_f(t)/D_0$ and $B_{\text{DRVT}}(t) = D'_f(t)/D(t_0)$ [12]. Finally, Eq.(23) shows that the TESE may be expressed as the summation of the DESE and the IESE. The quantity of IESE is a

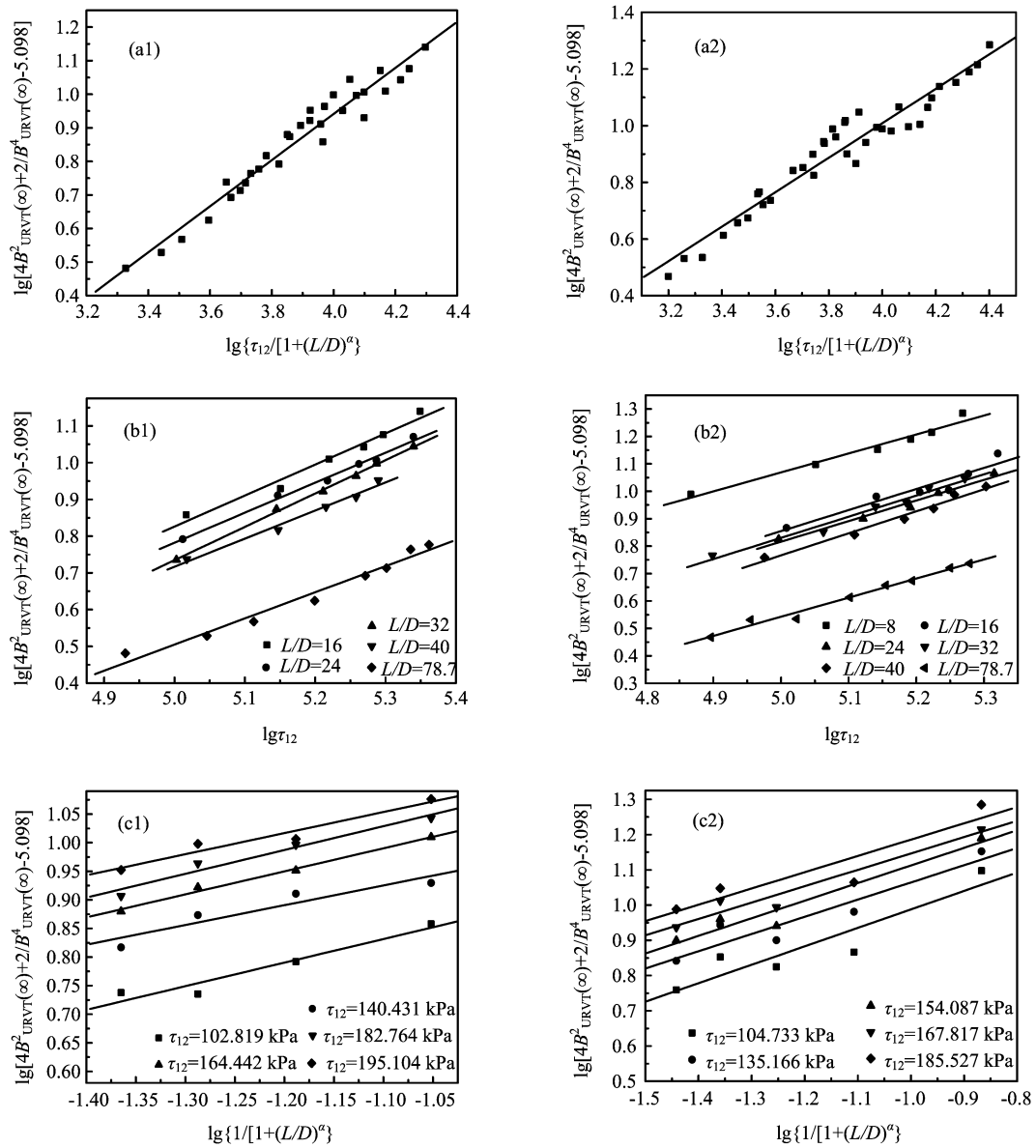


FIG. 4 Dependence of $\lg \left[4B_{URVT}^2(\infty) + \frac{2}{B_{URVT}^4(\infty)} - 5.098 \right]$ on $\lg \frac{\tau_{12}}{1 + (L/D)^\alpha}$, $\lg \tau_{12}$, and $\lg \frac{1}{1 + (L/D)^\alpha}$ HDPE at different temperature. (1) $T=200^\circ\text{C}$, (2) $T=220^\circ\text{C}$.

limited time-independent constant; its magnitude is determined by the molecular parameters of liquids and the operational variables of extrusion. These experimental methods and procedures are, respectively, given in the references [12,16-18].

B. Determination of molecular parameters of n' , α , η_0 , G_N^0 , and $1 - \overline{W}_\dot{\gamma}$ for HDPE [15]

Eq.(54) and (55) shows that the parameters of n' , α , η_0 , and G_N^0 can be determined, respectively, 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 $\ln \dot{\gamma}$. Then the parameters of n' , α , η_0 , and G_N^0 for all samples were determined from the slope and intercept of the lines with Eq.(54) and (55). The values for all samples are given in Table I.

$$\ln[\eta(\dot{\gamma})] = \frac{n'}{n' + 1} \ln[\psi_1(\dot{\gamma})] + \frac{n'}{n' + 1} \ln \frac{G_N^0}{(2n')^{n'}} \quad (54)$$

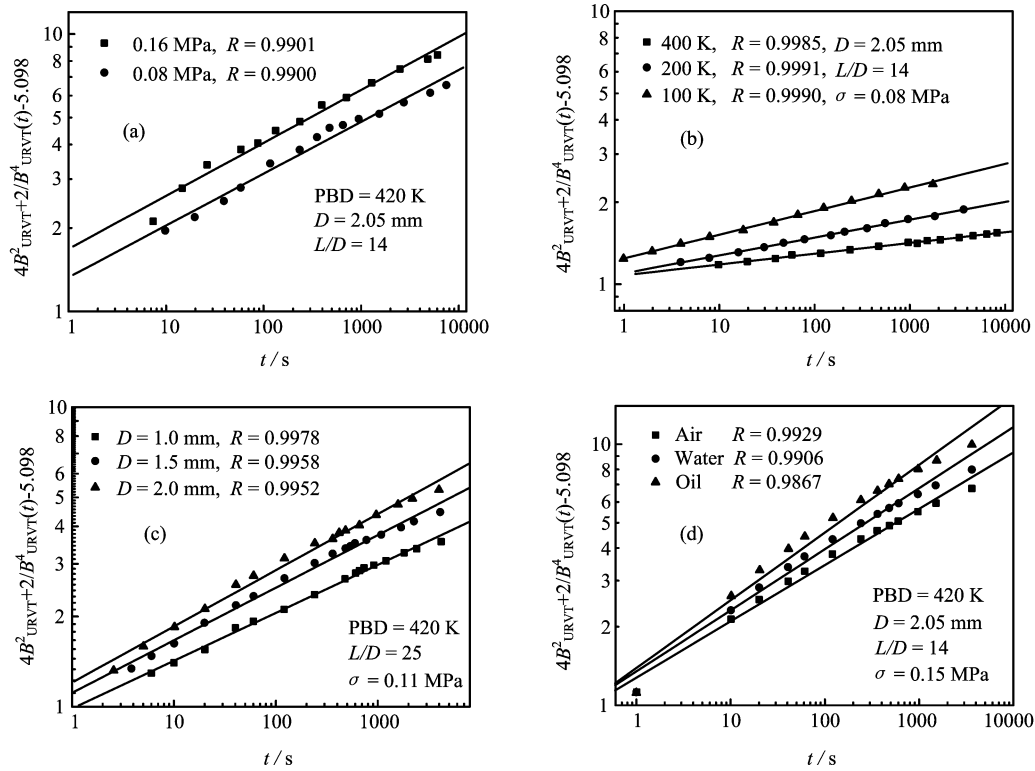


FIG. 5 Dependence of $\lg \left[4B_{\text{URVT}}^2(t) + \frac{2}{B_{\text{URVT}}^4(t)} - 5.098 \right]$ on $\lg t$ for the extrude swell of PBD.

TABLE I The molecular parameters of linear viscoelasticity for HDPE

Polymers	$\eta_0/(\text{kPa} \cdot \text{s})$	G_N^0/kPa	α	n'	$\langle 1 - \overline{W}_{\dot{\gamma}} \rangle$	$\overline{W}_{\dot{\gamma}}$
HDPE (200 °C)	116	20	0.84	0.84	0.484	0.516
(220 °C)	120	17	0.89	0.81	0.477	0.523

$$\ln \left[\frac{d \ln (\eta / \psi_1)}{d \ln \dot{\gamma}} \frac{\eta}{\psi_1} \right] = \alpha \ln \dot{\gamma} + \ln \left(\frac{\alpha}{2n'} \right) + \left(\alpha - \frac{1}{n'} \right) \ln \frac{\eta_0}{G_N^0} \quad (55)$$

Taking the logarithm on both sides of Eq.(19), there are

$$1 - \overline{W}_{\dot{\gamma}} = \frac{\ln \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{W} \right]_{S.F}^{\tau_{12}}}{\ln \left[\frac{n' (\eta_0 / G_N^0)^{1/n'} \dot{\gamma}}{1 + (L/D)^\alpha} \right]} \quad (56)$$

Eq.(56) shows that the fraction of recoverable conformations $1 - \overline{W}_{\dot{\gamma}}$ for each sample at the state of $\dot{\gamma}$ and $t_r = \infty$ can be directly calculated from the $\ln \left[\frac{1}{2} \left(\frac{N_1}{\tau_{12}} \right)_{W} \right]_{S.F}^{\tau_{12}}$, the molecular parameters n' , α , η_0 , and G_N^0 and the operating variables (N_1/τ_{12} , $\dot{\gamma}$, and L/D) with Eq.(56). Then, the average values of the fraction for the recoverable conformations averring over the whole numbers

of $\dot{\gamma}$ and L/D are also calculated with the following equations:

$$\langle 1 - \overline{W}_{\dot{\gamma}} \rangle = k = \sum_{l=1}^m \frac{\overline{A}_{\dot{\gamma}l}}{m} \quad (57)$$

$$\overline{A}_{\dot{\gamma}} = \sum_{i=1}^n \frac{1 - \overline{W}_{\dot{\gamma}}}{n} \quad (58)$$

where the numbers n and m are the whole number of $\dot{\gamma}$ and L/D . The average values of $\langle 1 - \overline{W}_{\dot{\gamma}} \rangle$ averring 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 0.484 and 0.477, as shown in Table I. They show that their average values approach to 1/2, or their average values are situated at the iso- or linear-viscoelastic state $\langle 1 - \overline{W}_{\dot{\gamma}} \rangle \doteq 1/2$. Their die swelling behaviors may be approximately considered as iso-die swelling behavior.

TABLE II Viscoelastic parameters of B_0 , A_0 , and A_{10} for PBD

Figure 4		B_0	A_0	$ \lg t_0 $	A_{10}	R	
(a)	0.08 MPa	0.1869	0.1231	0.5086*	0.0280	0.9900	PBD=420 K, $D=2.05$ mm, $L/D=14$
	0.16 MPa	0.1911	0.2256	0.5686*	0.1169	0.9901	
(b)	100 K	0.0866	0.0948	3.3372*	-0.1942	0.9990	$D=2.05$ mm, $L/D=14$, $\sigma=0.08$ MPa
	200K	0.0655	0.0401	2.4559*	-0.1208	0.9991	
	400K	0.0394	0.0329	1.6198*	-0.0309	0.9985	
(c)	$D=1.0$ mm	0.1600	-0.0066	0.3141	-0.0569	0.9978	PBD=420 K, $L/D=25$, $\sigma=0.11$ MPa
	$D=1.5$ mm	0.1756	0.0462	0.4665	-0.0357	0.9958	
	$D=2.0$ mm	0.1877	0.0803	0.5073	-0.0149	0.9952	
(d)	Air	0.2155	0.1061	0.4514	0.0088	0.9929	PBD=420 K, $D=2.05$ mm, $L/D=14$, $\sigma=0.15$ MPa
	Water	0.2339	0.1220	0.3891	0.0310	0.9906	
	Oil	0.2593	0.1430	0.3062	0.0636	0.9867	

Note: the data marked by * in the $|\lg t_0|$ column were taken from experimental value t_0 of Wang in reference [12], the other data in the $|\lg t_0|$ column were calculated with the Eq.(90) in Ref.[9].

C. The universal equation on the logarithmic correlation between TESE and the growth time for the different polymeric liquids at different operational variables

Eq.(30) were used to process the following experimental data of the PBD sample: (i) PBD with different molecular weights (1×10^5 , 2×10^5 , and 4×10^5) at a given operational variable ($D=2.05$ mm, $L/D=14$, and $\sigma=\tau_{12}=0.08$ MPa). (ii) PBD with a given molecular weight (4.2×10^5) at the different operational variables ($\sigma=\tau_{12}=0.16$ MPa and $\tau_{12}=0.08$ MPa). (iii) PBD with a given molecular weight (4.2×10^5) at the different operational variables ($D=1.0$, 1.5 , and 2.0 mm). (iv) PBD with a given molecular weight (4.2×10^5) at the different dispersing medium (air, water, and oil).

Eq.(30) shows that a series of lines were obtained for all PBD samples with the different molecular weights at the different operational variables.

These lines are drawn in Fig.4. The parameters of A_0 and B_0 for all PBD samples were, respectively, determined from the slopes and intercepts of the series lines. Then the values of A_{10} for all PBD samples were estimated with Eq.(35) and a given t_0 . These values of A_0 , B_0 , A_{10} , and their linear correlation coefficients R for all PBD samples are given in Table II.

The comparison of the theoretical equation of (TESE) with the experimental data of PBD are given in the above section C. The following facts can be manifested by these results: (i) There is a linear correlation between the $\lg \left[4B_{URVT}^2(t) + \frac{2}{B_{URVT}^4(t)} - 5.098 \right]$ and the $\lg t$, and a series of lines is obtained by plotting the $\lg \left[4B_{URVT}^2(t) + \frac{2}{B_{URVT}^4(t)} - 5.098 \right]$ against the $\lg t$ for PBD with the different molecular weights and a given \bar{M}_e (or concentration) at the different operational variables (τ_{12} , L/D , and different dispersing medium); (ii) From Eqs.(36), (38), (39), and Table II, it is easy to see

that the magnitudes of A_{10} and B_0 increase with an increasing of \bar{M}_W for mono polymers ($\bar{M}_w/\bar{M}_n=1$); (iii) From Eqs.(36), (38), and Table II, it is easy to see that the magnitudes of A_{10} and B_0 increase with an increasing of τ_{12} ; (iv) Experimental results show that the magnitudes of A_{10} and B_0 for the PBD samples at the different operational variables ($D=1.0$, 1.5 , and 2.0 mm) are 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 of $\frac{F_V}{F_S} = \frac{\pi D^2 L}{4\pi D L} = \frac{\pi D^3 k}{4\pi D^2 k} = \frac{D}{4}$ (for $L/D=k$). By replacing the expression of the constant ratio of L/D with the different F_V/F_S , then the expression of B_0 and A_{10} may be rewritten as

$$B_0 = \frac{2.303f(0)n_T}{1-f_e} \left(\frac{G_N^0}{\eta_0} \right)^{1/n'} \left[1 + \left(\frac{D}{4} \right)^\alpha \right] \quad (59)$$

$$A_{10} = (1 - \bar{W}_i) \cdot \lg \left\{ \frac{n' (1/G_N^0)^{1/n'} \tau_{12}}{[1 + (D/4)^\alpha] \eta_0^{(1-1/n')}} (1 - f_e) \right\} \quad (60)$$

Thus, from Table II and the above expressions of A_{10} and B_0 , it is easy to see that the magnitudes of B_0 increase with increasing of D for $L/D=25$, but the magnitudes of A_{10} decrease with an increasing of D for $L/D=25$; (v) From Eqs.(36), (38), (39), and Table II, it is easy to see that the magnitudes of A_{10} and B_0 increase with an increasing of the \bar{M}_e in the different dispersing medium (from air to oil); (vi) Eq.(30) can be successfully used to characterize the correlation of the total die swell effects to t , the molecular parameters (η_0 , G_N^0 , $1 - \bar{W}_i$, \bar{M}_W , and \bar{M}_e), the operational variables (D , L/D , τ_{12} , and dispersing medium).

TABLE III Viscoelastic parameters of HDPE

$T/^\circ\text{C}$	L/D	A_1	B_1	R	τ_{12}	A_2	B_2	R
200	16	0.8442	-3.3948	0.9868	102818.7	0.4124	1.2852	0.9668
	24	0.8170	-3.3025	0.9959	140431.0	0.3454	1.3051	0.9401
	32	0.9071	-3.8007	0.9991	164441.8	0.4025	1.4328	0.9959
	40	0.7650	-3.1084	0.9915	182763.7	0.4159	1.4863	0.9815
	78.7	0.7115	-3.0523	0.9867	195103.9	0.3594	1.4590	0.9725
		$\bar{A}_1=0.8090$				$\bar{A}_2=0.3889$		
220	8	0.6912	-2.3871	0.9851	104732.7	0.5234	1.5111	0.9249
	16	0.7688	-2.9892	0.9544	135165.7	0.4880	1.5523	0.9424
	24	0.7516	-2.9419	0.9890	154087.1	0.4995	1.6119	0.9707
	32	0.7730	-3.0349	0.9877	167817.0	0.4643	1.6107	0.9731
	40	0.8038	-3.2525	0.9902	185526.6	0.4620	1.6477	0.9239
	78.7	0.6969	-2.9417	0.9921				
		$\bar{A}_1=0.7476$				$\bar{A}_2=0.4874$		

TABLE IV Viscoelastic parameters of HDPE

$T/^\circ\text{C}$	$A_S = (1 - \bar{W}_{\dot{\gamma}})_S$		$B = \langle 1 - \bar{W}_{\dot{\gamma}} \rangle \lg \frac{n' (\eta_0/G_N^0)^{1/n'}}{\eta_0}$		R
	A_S^a	A_α^b	B_{Exp}^c	B_{Th}^d	
200	0.6871	0.5990	-1.8071	-2.0471	0.9750
220	0.6083	0.6175	-1.4245	-1.9683	0.9664

^a From the slope of the line with Eq.(41).

^b $A_\alpha = (\bar{A}_1 + \bar{A}_1)/2$. From the average slope of the line with Eq.(45) and (49).

^c From the intercept of the line with Eq.(41).

^d Calculation from n' , η_0 , $\langle 1 - \bar{W}_{\dot{\gamma}} \rangle$, and G_N^0 was given in Table I.

D. The universal equation on the logarithmic correlation between UESE and the operational variables for a given polymeric liquid

Eq.(41) was used to treat the experimental data for HDPE at two different temperatures (200 and 220 °C). Two lines are obtained by plotting y against $\lg \frac{\tau_{12}}{1 + (L/D)^\alpha}$; they are given in Fig.5 (a1) and (a2).

The parameters of A_S and B averring over the whole pairs between τ_{12} and L/D were determined from the slope and intercept of the lines by plotting y against $\lg \frac{\tau_{12}}{1 + (L/D)^\alpha}$ with Eq.(41). Their values of A_S , B , and their inter-correlation coefficient R for HDPE at temperatures (200 and 220 °C) are all given in Table III.

Eq.(45) shows that a series of lines can be obtained by plotting y against $\lg \tau_{12}$ for HDPE at two different temperatures (200 and 220 °C). They are given in Fig.5 (b1) and (b2).

The parameters of A_1 and B_1 averring over the whole numbers of τ_{12} for HDPE at temperatures (200 and 220 °C) were determined from the slopes and intercepts of the series of lines shown in Fig.5 (b1) and (b2). The values of A_1 , B_1 , and their inter-correlation coefficients

are all given in Table III. The average values of \bar{A}_1 averring over the whole numbers of L/D was also calculated. They are also given in Table III.

Eq.(49) shows that a series of lines can be obtained by plotting y against $\lg \frac{1}{1 + (L/D)^\alpha}$ for HDPE at two different temperatures (200 and 220 °C). They are given in Fig.5 (c1) and (c2). The parameters of A_2 , B_2 , averring over the whole numbers of L/D for HDPE at temperatures (200 and 220 °C) are determined from the slopes and intercepts of the series of lines with Eq.(49). The values of A_2 and B_2 and their R are all given in Table III. The average values of \bar{A}_2 averring over the whole numbers of τ_{12} were also calculated. They are also given in Table III.

Eq.(52) shows that two lines can be obtained by plotting B_1/A_1 against $\lg \frac{1}{1 + (L/D)^\alpha}$ for HDPE samples at two temperatures (200 and 220 °C). They are given in Fig.6(a). Eq.(53) shows that two lines can be obtained by plotting B_2/A_2 against $\lg \tau_{12}$ for HDPE samples at two temperatures (200 and 220 °C). They are given in Fig.6(b).

The results can be used to establish: (i) There is a linear correlation between $\lg \frac{\tau_{12}}{1 + (L/D)^\alpha}$

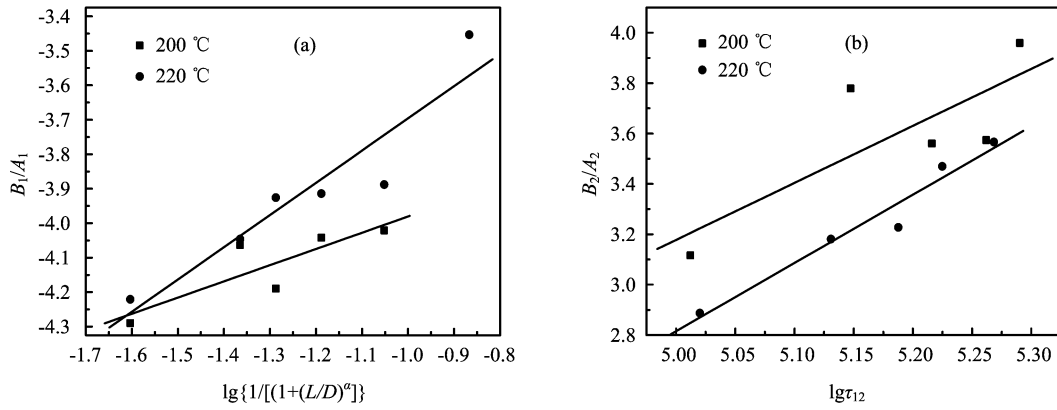


FIG. 6 Dependence of B_1/A_1 and B_2/A_2 on $\lg \frac{1}{1+(L/D)^\alpha}$ and $\lg \tau_{12}$ for the extrude swell of HDPE.

and $\lg \left[4B_{URVT}^2(\infty) + \frac{1}{2B_{URVT}^4(\infty)} - 5.098 \right]$, between $\lg \tau_{12}$ and $\lg \left[4B_{URVT}^2(\infty) + \frac{1}{2B_{URVT}^4(\infty)} - 5.098 \right]$ for a given $1 + \frac{L}{D}^\alpha$, between $\lg \left[4B_{URVT}^2(\infty) + \frac{1}{2B_{URVT}^4(\infty)} - 5.098 \right]$ and the $\lg \frac{1}{1+(L/D)^\alpha}$ for a given τ_{12} . There is a series of lines obtained by plotting $\lg \frac{\tau_{12}}{1+(L/D)^\alpha}$ against $\lg \left[4B_{URVT}^2(\infty) + \frac{1}{2B_{URVT}^4(\infty)} - 5.098 \right]$, $\lg \left[4B_{URVT}^2(\infty) + \frac{1}{2B_{URVT}^4(\infty)} - 5.098 \right]$ against $\lg \tau_{12}$, $\lg \left[4B_{URVT}^2(\infty) + \frac{1}{2B_{URVT}^4(\infty)} - 5.098 \right]$ against $\lg \frac{1}{1+(L/D)^\alpha}$. (ii) There is a linear correlation between B_1/A_1 and $\lg \frac{1}{1+(L/D)^\alpha}$, and between B_2/A_2 and $\lg \tau_{12}$. (iii) For HDPE at two temperatures the values of parameters A_S and B_{Exp} were determined from the slopes and intercepts of the lines by plotting $\lg \left[4B_{URVT}^2(\infty) + \frac{1}{2B_{URVT}^4(\infty)} - 5.098 \right]$ against $\lg \frac{\tau_{12}}{1+(L/D)^\alpha}$ with Eq.(41). They are identified with the value of \bar{A}_a which is obtained with the relation of $(\bar{A}_1 + \bar{A}_2)/2 = \bar{A}_a$ and the value of B_{Th} which is calculated from the linear viscoelastic parameters (n' , α , η_0 , G_N^0 , and $\langle 1 - \bar{W}_{\dot{\gamma}} \rangle$). These agreements provide a verification for the new dynamic theory of die swell in the extrudates. This shows that the dynamic theory of die swell can be successfully used to characterize the correlation of the UESE to the molecular parameters (n' , α , η_0 , G_N^0 , and $\langle 1 - \bar{W}_{\dot{\gamma}} \rangle$) and the operational variables (τ_{12} and L/D).

IV. CONCLUSION

(i) The dynamic theory of die swell deduced in a previous paper was extensively applied to study the extrudate swelling behaviors of HDPE and PBD in a simple shear flow at a steady shear stress. In the course of recovery, two recovery regions and three growth stages may be divided, and the free recoil and these extrudate swelling effects may be expressed as the function of shear stress.

(ii) The correlation of instantaneous $t_r=0$, delayed $t_r=t$, total $t_r=t$, and ultimate $t_r=\infty$ extrudate swelling effects to the molecular parameters and the operational variables at the steady shear stress were derived from the dynamic theory of die swell. Two sets of universal equations for the total and ultimate extrudate swelling effects were also deduced.

(iii) The first universal equation of the logarithmic correlation between the total extrudate swelling effect [TESE] and the growth time under the free and steady shear stress state was verified by experimental data of PBD with different molecular weights and different operational variables.

(iv) The second universal equation of the logarithmic correlation between the ultimate extrudate swelling effect [UESE] and the operational variables under the free and shear stress state was verified by experimental data of HDPE at two temperatures and different operational variables. The two universal equations are in excellent agreement with the experimental results.

(v) The excellent agreement results show that the two universal equations can be directly used to predict the correlations of the time-dependent and time-independent (or ultimate) extrudate swelling behaviors to the molecular parameters (n' , α , η_0 , G_N^0 , and $\langle 1 - \bar{W}_{\dot{\gamma}} \rangle$) and the operational variables (τ_{12} and L/D) and the growth time t .

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