# The Dependence of Shear and Elongational Viscosity on the Molecular Weight of Poly(vinylidene fluoride)

### T. KOIZUMI, S. USUI

Nishiki Research Laboratories, Kureha Chemical Industry Co. Ltd., 16 Ochiai, Nishiki-machi, Iwaki-city, Fukushima 974-8686, Japan

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**ABSTRACT:** The dependence of shear and elongational viscosity on the molecular weight of poly(vinylidene fluoride) has been studied using a capillary rheometer. The elongational viscosity was evaluated based on Cogswell's method with two types of capillaries: capillary length (L)/capillary diameter (D) = 10 mm/1 mm and L/D = 0 mm/1 mm. We used the ratio  $P_0/P_L$  that indicates the contribution of elongational flow to the total flow involving both the shear and elongational flows.  $P_L$  and  $P_0$  are the pressure losses in the capillary and the converging flows, respectively.  $P_0/P_L$  increased with molecular weight and shear rate. This corresponds to decreasing the number of entanglements of molecular chain under a large displacement, especially high shear. Thus, we suggest using  $P_0/P_L$  as the parameter of the entanglement interaction on the molecular chain under a large displacement. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2381–2384, 1999

Key words: PVDF; shear viscosity; elongational viscosity; molecular weight

# **INTRODUCTION**

Injection and/or extrusion are generally used to mold polymer materials. Shear flow is commonly shown in injection and extrusion molding, such as the flow in the cavity, in the cylinder, and so on. The flows of the melt front and in the converging region are a typical elongational flow. Thus, it is important to evaluate both the shear and elongational viscosity to understand flow properties during injection and extrusion molding.

A capillary rheometer is commonly used to evaluate the shear viscosity of polymer melt. In 1972,<sup>1,2</sup> Cogswell proposed a simple method for measuring both the shear and elongational viscosity using a capillary rheometer. This method was based on the assumption that the entry pressure loss from the reservoir to the capillary was due to elongational flow. Although Cogswell's method did not receive much attention in the literature of the 1980s,<sup>3-8</sup> there were many studies using Cogswell's method<sup>9-11</sup> because of its simplicity in recent years.

For this article, we evaluated the dependence of the shear and elongational viscosity on the molecular weight of poly(vinylidene fluoride) (PVDF) using Cogswell's method. PVDF is known for its excellent chemical residence and good electrical properties. Its high dielectric constant permits its use in some applications. Recently, PVDF has been used as pipes for ultra-pure-water uses. But, the melt viscoelasticity of PVDF did not receive much attention in the literature.<sup>12</sup> Thus, the purpose of this article is to discuss the entanglement interaction of the molecular chain under a large displacement by comparing both shear and elongational flows.

Correspondence to: T. Koizumi.

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Table IMolecular Weight of PVDF

|        | ${M}_n$ | $M_w$   |
|--------|---------|---------|
| PVDF-1 | 108,000 | 222,000 |
| PVDF-2 | 128,000 | 265,000 |
| PVDF-3 | 147,000 | 302,000 |

# **EXPERIMENTAL**

#### **Materials**

The molecular weights of PVDF used in this study are shown in Table I. PVDF was polymerized from vinylidene fluoride using dinormalpropoxy peroxy dicarbonate as an initiator. The molecular weight of PVDF was measured by size permeation chromatography with a flame ionization detector at room temperature in dimethylamide 0.2 wt % solvent. The calibration curve of size permeation chromatography was determined by polystyrene standard.

#### **Rheological Measurement**

Rheological measurements were conducted using a capillary rheometer manufactured by Toyo Seiki Co., Ltd., at a temperature of 200°C. We calculated the shear and elongational viscosity using Cogswell's method. To evaluate the elongational viscosity, we prepared two capillaries; the first capillary was comprised of a cylindrical constant radius capillary (10 mm length and 1 mm diameter), and the second capillary was comprised with nearly 0 mm length and 1 mm diameter. The die angle of the capillaries was 180° because the effect of the elongational flow was the largest at the angle.  $P_L$  and  $P_0$  are the pressure losses measured using L/D = 10 mm/1 mm and L/D = 0 mm/1 mm, respectively.

#### **RESULTS AND DISCUSSION**

The flow curve of PVDF-2 is shown in Figure 1. The figure shows a typical shear flow curve over the range of shear rates in excess of two decades using L/D = 10/1 capillary. Since the flow curves showed nonlinearity, the flow curve data were fitted by the following equation using a least-squares method.

$$\log \sigma = a_1 (\log \dot{\gamma})^2 + a_2 \log \dot{\gamma} + a_3 \tag{1}$$

where  $a_1$ ,  $a_2$ , and  $a_3$  are the fitting parameters, and  $\dot{\gamma}$  and  $\sigma$  is the shear rate and shear stress, respectively.

$$\sigma = \frac{P_L r}{2L} \tag{2}$$

The power law index n is calculated by the differentiation of eq. (1).

$$n = 2a_1(\log \dot{\gamma}) + a_2 \tag{3}$$

We calculated  $P_L$  as a function of shear rate from the fitting eq. (1). As shown in the figure, data were well fitted by the quadratic equation within the experimental shear rate range. Because similar trends were obtained for the other specimens, we calculated  $P_L$  at a given shear rate from the fitted quadratic equation. The shear rate dependence of  $P_0$  of PVDF-2 is also shown in Figure 2. Experimental data of  $P_0$  were well fitted by a quadratic equation, as well as the shear stress for all specimens. We calculated  $P_0$  by the same procedure described herein.

The shear rate dependence of shear viscosity with molecular weight is shown in Figure 3. As can be seen, the dependence of the shear viscosity on the shear rate of all samples measured showed non-Newtonian.



**Figure 1** Flow curve of PVDF-2, with L/D = 10/1 at 200°C.





**Figure 2** Dependence of  $P_0$  on the shear rate of PVDF-2, with L/D = 10/0 at 200°C.

The elongational rate dependence of elongational viscosity with molecular weight is shown in Figure 4. As can be seen, the elongational viscosity also increased with molecular weight.

As described in the Introduction,  $P_L$  is involved in the effects on both the shear and elongational flow, whereas  $P_0$  is involved in the effect of elongational flow only. As a result,  $P_0/P_L$  represents the ratio of elongational flow to the total flow. Figure 5 shows  $P_0/P_L$  as a function of the shear rate. Although it seemed that the quadratic equation fitting would affect a gentle curvature of the curves of the shear rate dependence of  $P_0/P_L$ , our conclusions were not affected by this curvature problem. As shown in the figure,  $P_0/P_L$  increased



**Figure 3** Shear rate dependence of shear viscosity with molecular weight at 200°C. ( $\bullet$ ) PVDF-1. ( $\blacktriangle$ ) PVDF-2. ( $\blacksquare$ ) PVDF-3.



**Figure 4** Elongational viscosity at 10 s<sup>-1</sup> of shear rate as a function of number average molecular weight. ( $\bullet$ ) PVDF-1. ( $\blacktriangle$ ) PVDF-2. ( $\blacksquare$ ) PVDF-3.

with molecular weight and shear rate. The increase of  $P_0/P_L$  with molecular weight suggests that the molecular weight dependence of elongational viscosity is large, compared with that of shear viscosity.

We thought these results were related to the entanglement of the molecular chain. Namely,  $P_0/P_L$  increased with the molecular weight because the molecular chains were well-entangled, and the number of entanglements per molecular chain increased with molecular weight. In addition,  $P_0/P_L$  increased under a large displacement, because the chains were unable to disentangle. Consequently, we think that the molecular de-



**Figure 5** Shear rate dependence of  $P_0/P_L$ . (•) PVDF-1. (•) PVDF-2. (•) PVDF-3.

pendence of  $P_0/P_L$  would be a good parameter of the entanglement interaction of the molecular chain under a large displacement. The reason is shown as follows.

The plateau modulus  $G_N^0$  that is measured under a small displacement is usually used as the parameter of molecular entanglement. The concept of  $G_N^0$  of linear polymer is based on the rubber elastic theory. It is assumed that the structure of molecular entanglement does not change under a small displacement in the linear viscoelastic region. But, it is known that the original entanglement structure changes are in excess of a certain critical displacement.<sup>13-15</sup> Thus, the elastic parameter,  $G_N^0$ , of linear viscoelastic theory is not proper under a large displacement because injection or extrusion is performed under a high shear and elongational displacement. Thus, the viscoelastic characteristics of polymer melts in view of processing should be evaluated under a large displacement.

Although conventional apparatus to measure the elongational viscosity has been invented,<sup>16,17</sup> there are a lot of problems in measuring the elongational viscosity (e.g., the difficulty of sample preparation, the impossibility of measuring a low viscosity material, and so on). On the other hand, Cogswell's method is easy to evaluate the elongational viscosity related to the elastic character under a large displacement, although surely the elongational viscosity of this method is a little complicated. Thus, we think  $P_0/P_L$  would be the parameter as the entanglement interaction on the molecular chain under a large displacement.

# **CONCLUSIONS**

We studied the dependence of shear and elongational viscosity on the molecular weight of PVDF using a capillary rheometer. Elongational viscosity was evaluated based on Cogswell's method using two types of capillaries: L/D = 10 mm/1mm and L/D = 0 mm/1 mm.  $P_0/P_L$  increased with the molecular weight and shear rate. The molecular dependence of  $P_0$  is small, compared with that of  $P_L$  because the numbers of entanglement decrease under a large displacement, especially high shear. Thus, we suggest that  $P_0/P_L$ would be the parameter as the entanglement interaction on the molecular chain under a large displacement.

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