論文

A Comparative Study of Flow Instabilities in Extrusion, Melt Spinning, and Tubular Blown Film Extrusion of Rheologically Characterized High Density, Low Density and Linear Low Density Polyethylene Melts

by

Hideki YAMANE* and James L. WHITE

*Polymer Engineering Center, University of Akron,
Akron, Ohio 44325, U.S.A.*

ABSTRACT

A comparative study of the (i) extrusion, (ii) melt spinning and (iii) tubular film instabilities of a range of high density, linear low density and low density polyethylene melts is presented. The unique features of the unstable behavior are described for each of these operations. Linear (including linear low density) polyethylenes generally exhibit a slip induced extrusion instability and often several regimes of unstable flow. Long chain branched polyethylenes generally exhibit more stable melt spinning and tubular film characteristics than the linear polyethylenes. Broadening molecular weight distribution of linear polyethylene destabilizes melt spinning behavior, but stabilizes tubular film extrusion. The influence of rheological properties on these instabilities is discussed.

* Present Address: *Dept. of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto, Japan*

Key words: Polyethylene/Extrusion instabilities/Draw resonance/Tubular film Instabilities/Molecular weight distribution/Long chain branching

(原稿受理：1986年11月5日)

INTRODUCTION

Many instabilities have been described through the years in polymer melt processings. The earliest of these phenomena to be discovered and investigated were instabilities in extrusion through dies^{1~8}). These occur at a critical extrusion rate or die wall shear stress^{2~6}). Post die flow instabilities have been observed in various polymer processing operations including melt spinning^{9~17}), cast film extrusion^{11,18~20}), and tubular film extrusion (Figure 1)^{18,21~23}). In both melt spinning and cast film, melt is pulled down from a die under uniaxial tension into a quench bath. Tubular film extrusion involves a simultaneous inflation and drawdown which are associated with a biaxial state of stress. Many researchers have noted that the instabilities occurring in melt spinning and cast film

are essentially the same with periodic variations in thickness occurring suddenly at a critical drawdown ratio. The tubular film instabilities are quite different with the onset of different periodic motions being more closely associated with variations in bubble blowup ratio.

In most cases, published investigations involve the occurrence of individual instabilities in uncharacterized polymer melts. The present study compares the die extrusion, melt spinning and tubular film processing instability behavior of a series of molecularly and rheologically characterized polyethylene melts of varying type. These include high density, low density and linear low density polyethylene melts. Some of the polymers are part of the International Union of Pure and Applied Chemistry (IUPAC) Working Party on Commercial Polymers Program²⁴).

A total of six polyethylenes were included in this study, three of which were high density polyethylenes (HDPE), two

* 山根秀樹, 京都工芸繊維大学繊維学部高分子学科
〒606 京都市左京区松ヶ崎御所海道町

Table I. Materials investigated in this study

material designation	source	density
HDPE-1*	Hoechst GM 9255F	0.939-0.942
HDPE-2*	Hoechst GF 7750M	0.944-0.946
HDPE-3*	Dupont Alathon 7030	0.950-0.953
LLDPE-1*	Cdf Chimie FN 1290	0.920-0.921
LLDPE-2	Union Carbide GRSN-7047	0.918
LLDPE-3	Union Carbide PFDA 7540	0.920
LDPE-1*	BP Chemicals DYNK 6	0.917-0.918
LDPE-2*	BP Chemicals DXM 430	0.921
LDPE-3	Chemplex 1007	0.919

* IUPAC Sample

were low density (LDPE) and one was a linear low density polymer (LLDPE). The melt rheological and structural characteristics of these polymers have been described in an earlier paper²⁵⁾ and will only briefly be summarized here. This is given in Table I.

Extrusion

The extrusion characteristics of the polyethylenes were investigated using a Monsanto Processability Tester Capillary Rheometer at 190°C. Dies of diameter 1.5mm and length-diameter ratios of 5 and 20 were used.

Extrudate swell was characterized in the following manner. The melts were extruded through dies until the extrudate reached 2.5cm in length. It was then cut from the die exit. The extrudate was then cooled in the air and the diameter of the extrudate at 1.0cm from the lower edge was measured. Density corrections were made between room temperature and 190°C. The cooled extrudate samples were also annealed in silicone oil at 160°C for 20 minutes and the diameters were measured.

Extrudate swell, B , is defined as

$$B = D_e/d$$

where D_e is the diameter of the extrudate and d is that of the die.

Extrudate distortion was investigated employing dies of diameter 0.76mm and L/D 30 and of 1.5mm and L/D 20. For extrusion rate, the total pressure was recorded and the extrudate was taken as a sample. In this experiment the minimum increment of the die wall shear rate was 27.8 sec⁻¹ for the die of 0.76mm diameter, and 3.6 sec⁻¹ for the die of diameter 1.5mm. Extrusion rate was increased gradually until either pressure fluctuations or irregularities in the extrudate diameter were observed. Once any extrudate distortion was

Fig. 1 Schematic diagrams of die extrusion, melt spinning and tubular blown film extrusion.

observed, the extrusion rate was decreased, and then increased again to try to accurately determine the condition of onset.

The mode of extrudate irregularity was observed for each material over a range of extrusion rates.

Melt Spinning

Melt spinning experiments were carried out using an Instron Capillary Rheometer. For isothermal melt spinning a die of diameter 1.07mm and L/D of 28.9 was used. Two isothermal chambers were used. These had lengths of 2.5cm and 7.0cm. They were placed below the die. The filament moved through the chamber into quench bath.

In the non-isothermal experiment a die of diameter 1.27mm and L/D ratio of 27.7 was used. An air gap of 2.5cm between the die exit and the quench bath was used.

The fiber passed through the quench bath and was taken up on a rotating roll. A Rothschild tensiometer was placed near the take-up device.

The onset of instabilities was determined by the appearance of large amplitude fluctuations in the tensiometer trace.

Tubular Film Extrusion

Tubular film extrusion experiments were carried out in a 3/4 inch Killion screw extruder with a Killion tubular blown film system. The screw extruder had an annular blown film die of diameter 3.2cm with a gap of 1.0mm. The volumetric flow rate was 1500 cm³/hour. Bubbles were specified following Kanai and White²³⁾ and Minoshima and White¹⁸⁾ in terms of three control variables: drawdown ratio, V_L/V_0 , blowup ratio, R_L/R_0 , and frostline height, z_f .

The onset of instabilities was observed visually and recorded using a video camera.

EXTRUSION

Results

The frozen extrudate swell of the melts emerging from dies of L/D 5.0 and L/D 20 are shown in Fig. 2. These data have been corrected to 190°C. Generally swell decreases with increasing die L/D . For the large L/D die, the swell orders

Fig. 2 Extrudate swell of frozen extrudate as a function of die wall shear stress σ_{12} , low L/D die (top) and high L/D die (bottom).

at $32Q/\pi D^3$ of 7.2 sec^{-1} as

$$\text{LDPE-1} > \text{LDPE-3} > \text{LLDPE-3} > \text{HDPE-2} > \text{HDPE-1} \\ > \text{LDPE-2} > \text{LLDPE-1} \sim \text{LLDPE-2} \sim \text{HDPE-3}$$

A comparison at the same σ_{12} indicates a different ordering.

At σ_{12} of $5 \times 10^4 \text{ Pa}$, we have

$$\text{LDPE-3} > \text{LLDPE-3} > \text{LDPE-1} > \text{LDPE-2} > \text{HDPE-2} \\ > \text{LLDPE-2} \sim \text{HDPE-3} > \text{LLDPE-1} \sim \text{HDPE-1}$$

For the small L/D die at $32Q/\pi D^3$ of 7.2 sec^{-1} ,

$$\text{LDPE-3} > \text{LLDPE-3} > \text{LDPE-1} > \text{LDPE-2} > \text{HDPE-2} \\ > \text{HDPE-1} > \text{LLDPE-1} > \text{LLDPE-2} > \text{HDPE-3}$$

At the same σ_{12} ,

$$\text{LDPE-3} > \text{LDPE-1} > \text{LDPE-2} > \text{LLDPE-3} > \text{HDPE-2} \\ > \text{HDPE-1} > \text{HDPE-3} > \text{LLDPE-2} > \text{LLDPE-1}$$

The swell of the annealed extrudates is shown in Fig. 3.

The data order at the same $32Q/\pi D^3$ as:

$$\text{LLDPE-3} > \text{HDPE-2} > \text{LDPE-3} > \text{LDPE-1} > \text{HDPE-1} \\ > \text{LDPE-2} > \text{LLDPE-1} > \text{LLDPE-2} > \text{HDPE-3}$$

At the same σ_{12} the data indicate LLDPE-3 and LDPE-3 have the highest values, followed by HDPE-2, LDPE-1 and LDPE-2. LLDPE-1, LLDPE-2 and HDPE-3 have the lowest values.

Fig. 3 Swell of annealed extrudate. B versus σ_{12} (top) and B_a/B_u versus $32Q/\pi D^3$ (bottom).

We continued to characterize the extrusion process and observe extrudates at higher extrusion rates where flow instabilities occurred. Many of the melts investigated exhibited discontinuities in their pressure drop-extrusion rate curves. The data are summarized in Fig. 4. It may be seen that at a critical extrusion rate, pulsations occur. Extrudate distortion occurred in conjunction with these pulsations. The characteristics of the materials are divided into four groups in their behavior. These are

- i) HDPE-1 and HDPE-2
- ii) HDPE-3, LLDPE-1, and LLDPE-2
- iii) LLDPE-3
- iv) LDPE-1, LDPE-2, LDPE-3

The behavior was as follows. The first group (HDPE-1, HDPE-2) of materials exhibit three zones in their Δp versus $32Q/\pi D^3$ plots. In the low Q region, Δp shows a monotonic

Fig. 4 Pressure drop-extrusion rate $32Q/\pi D^3$ behavior.
 E.I. : onset of large scale extrusion instability
 S : onset of sharkskin type instability

(a) HDPE-1 (Group i)

(b) LLDPE-2 (Group ii)

(c) LLDPE-3 (Group iii)

(d) LDPE-2 (Group iv)

(e) Microscopic surface roughness on HDPE-1 extrudate.

(f) Microscopic surface roughness on LLDPE-3 extrudate.

(g) Matte phenomenon observed on LDPE-3 extrudate.

Fig. 5 Extrudate characteristics.

increase with Q . At a critical extrusion rate, there is a clear transition to a regime where a pulsation occurs. The shaded parts in the characteristic curves indicate this zone. At a higher extrusion rate, Δp again becomes a monotonically increasing function of Q . The characteristics of the extrudates are shown in Fig. 5. In the lowest extrusion rate region, the extrudates of HDPE-2 are smooth, while HDPE-1 has a microscopic surface roughness (Fig. 5-e). In the second zone where Δp shows a large pulsation, the extrudate has two distinctive parts: lengths where the surface is smooth and uniform, and lengths where the extrudate is distorted. In the third zone where the pulsation disappears, the extrudate becomes highly distorted.

The second group (HDPE-3, LLDPE-1, LLDPE-2) exhibit five distinct zones in their Δp - Q flow curves. At lower extrusion rates, the behavior is similar to that of HDPE-1 and HDPE-2. There is a region of smooth extrudate, followed by a pulsating region with smooth and rough sections, and a third regime with fairly smooth extrudate. At higher extrusion rates there is a second pulsation regime. In this zone, there are two distinctive distorted sections along the extrudate. At higher extrusion rates a uniform grossly distorted extrusion regime occurs.

The behavior of LLDPE-3 is again different. The extrudate is uniform with a microscopic roughness up to a critical extrusion rate (Fig. 5-f). No clear pulsation region is observed. The extrudate becomes increasingly rough as extrusion rate increases, evolving to a screw thread appearance.

The LDPEs exhibit different behavior. At very low Q , the extrudate is smooth and uniform. At a higher extrusion rate a fine scale roughness (matte) is observed with LDPE-3 extrudate (Fig. 5-g). No pulsation is observed and the Δp - Q curves are continuous. A helical extrudate is first observed in LDPE-2 and to a lesser extent in LDPE-1, but not in LDPE-3. At higher extrusion rates, the shapes of the LDPE-2 and LDPE-1 evolve from a helical shape to grossly distorted extrudates. The LDPE-3 becomes more grossly distorted.

Discussion

The onset of extrusion instabilities has been associated, since the studies of Spencer and Dillon²⁾ and Tordella^{4,6)}, with a critical shear stress. This has been found with the present polymers. Table II indicates the values of Q , Q/D and Q/D^3 for the polymers investigated. For all samples except for LDPE-1, only Q/D^3 values, which are proportional to $\dot{\gamma}_a$, are independent of the dies used and these can be taken as the critical values. Table III shows critical shear rates $\dot{\gamma}_c$ and critical shear stresses σ_c for these materials.

The shape of the extrudates in unstable extrusion seems to be most strongly affected by structural parameters such as molecular weight distribution and long chain branching.

Only HDPE-3, LLDPE-1 and LLDPE-2 show sharkskin type distortions. All of the linear polymers except for

Table II. Variation of Q , Q/D and Q/D^3 with onset of extrudate instability.

Polymer	$Q(\text{cm}^3/\text{sec})$		$Q/D(\text{cm}^2/\text{sec})$		$Q/D^3(1/\text{sec})$	
	Die-1	Die-2	Die-1	Die-2	Die-1	Die-2
HDPE-1	0.0194	0.168	0.255	1.12	44.2	49.8
HDPE-2	0.0152	0.134	0.200	0.893	34.7	39.7
HDPE-3	0.0560	0.671	0.737	4.47	128.0	199.0
LLDPE-1	0.0264	0.255	0.347	1.70	60.1	75.6
LLDPE-2	0.0217	0.208	0.286	1.39	49.5	61.7
LLDPE-3	0.108	0.823	1.42	5.49	246	244
LDPE-1	*	0.047	*	0.313	*	13.9
LDPE-2	0.0200	0.166	0.263	1.11	45.6	49.2
LLDPE-3	0.0095	0.121	0.125	0.805	21.6	35.8

* Extrusion instability occurs at any flow rate with this die.

Table III. Critical shear rates $\dot{\gamma}_c$ and critical shear stresses σ_c at the onset of extrusion instabilities for PE samples. (Die-1, $D=0.76\text{mm}$ and $L/D=30$)

Polymer	$\dot{\gamma}_c(\text{sec}^{-1})$	$\sigma_c \times 10^{-5}(\text{Pa})$
HDPE-1	450	2.95
HDPE-2	353	3.14
HDPE-3	1300	3.94
LLDPE-1	612	3.33
LLDPE-2	504	4.03
LLDPE-3	2502	402.00
LDPE-1	*	*
LDPE-2	464	1.32
LDPE-3	220	1.00

* Extrusion instability occurs at all flow rates with this die.

LLDPE-3 show stick-slip flow at the beginning of the instability. According to the supplier, LLDPE-3 contains small amounts of long chain branching. The extrusion characteristics of linear polymers are not found in this sample.

The onset of the extrusion melt flow instabilities has been associated both with "melt elasticity induced flow instabilities" and with "shear stress induced wall slippage". These have strong relation to a Weissenberg number²⁶⁾. Other explanations have been in terms of "melt fracture"^{3,4)}. Both mechanisms would be associated with a critical shear rate and a critical shear stress. Perhaps all are operative. The "melt elasticity" or "melt fracture" mechanism might be associated with the LDPEs. The slip induced mechanism might be associated with the HDPEs and LLDPEs. Flow visualization²⁷⁻²⁹⁾ and flow birefringence⁶⁾ studies have shown that the die entrance is the location of the instability in LDPE and the die wall is the site of the instability for HDPE. The mechanism of the extrusion instabilities, however, still remain largely unresolved.

MELT SPINNING

Results

All melt spun filaments are generally non-uniform, exhibiting a varying diameter along their length. At low drawdown ratios, these have a magnitude of 5~10% of their diameter. Above a critical drawdown ratio, V_L/V_0 , the spinline shows a periodically varying diameter of high amplitude. This would seem to be the "draw resonance" phenomenon^{19,20}. The critical value of V_L/V_0 differs from polymer to polymer and with the presence, or length of isothermal chambers. The results are summarized in Table IV. The ratio of maximum to minimum filament diameter, $D_{\max}/D_{\min}$, is plotted as a function of V_L/V_0 in Fig. 6.

Generally we see that decreasing the length of the isothermal chamber stabilizes the spinline. Greatly enhanced stabilization occurs by removing the chamber and letting the spinline air-cool.

The critical drawdown ratios for the different polymers studied generally order in the same manner for each set of conditions. This ordering is

$$\text{LDPE-2} > \text{LDPE-3} > \text{LDPE-1} \sim \text{LLDPE-1} \sim \text{LLDPE-2} \\ \sim \text{HDPE-3} > \text{LLDPE-3} > \text{HDPE-2} > \text{HDPE-1}$$

Discussion

Generally the experimental data for the onset of draw resonance order as follows:

Table IV. Critical drawdown ratios for onset of draw resonance, V_L/V_0

Sample	Isothermal Chamber (7cm)	Isothermal Chamber (2.5cm)	Non-Isothermal (2.5cm air gap)
HDPE-1	4.9	5.9	8.7
HDPE-2	6.7	8.2	14.4
HDPE-3	10.9	14.0	28.7
LLDPE-1	11.7	13.4	27.2
LLDPE-2	11.7	15.2	22.3
LLDPE-3	9.0	10.7	16.6
LDPE-1	15.2	14.0	23.5
LDPE-2	45.0	44.0	115.8
LDPE-3	39.2	37.5	filament breaks at 50

Fig. 6 $D_{\max}/D_{\min}$ as a function of drawdown ratio V_L/V_0 for isothermal melt spun fibers with air gap of 7.0cm.

This general type of behavior has been observed by earlier investigators. Ghijssels and Ente¹³, Minoshima et al.¹⁴ and Yamane and White¹⁵ have found that narrowing of molecular weight distribution stabilizes melt spinning behavior of polypropylenes. Minoshima and White¹⁶ have found similar behavior with polyethylenes of varying molecular weight distribution. In Fig. 7, we plot the critical values of V_L/V_0 versus M_w/M_n for our own data and those of Minoshima and White. HDPE, LLDPE and polypropylene results are included.

The stabilization of the fiber spinline by long chain branching has been reported by White and Yamane¹⁷ in an IUPAC working party study of polyethylene terephthalates. Minoshima and White¹⁶ describe a similar conclusion for long chain branched polyethylenes. Our own results are very similar. These results may be traced to rheological responses. Minoshima and White¹⁶ note that the critical V_L/V_0 correlates with the elongations to break found in uniaxial extension experiments. The suggestion for such an interpretation traces back to White and Ide¹² who argued that necking failures in uniaxial extension are similar in nature to draw resonance or better "draw resonance" is a continuous process equivalent of necking. The phenomena appear differently because the order of the differential equations describing draw resonance is higher. It is found that both necking failure and draw resonance are retarded by deformation rate hardening characteristics of melts. Thus the LDPEs which show striking strain hardening effects exhibit the most stable uniaxially stretched filaments and melt spinning behaviors.

Limiting to linear polymers, one finds that both shear and elongational viscosities respond similarly to the increase in breadth of molecular weight distribution. Both steady state shear and elongational viscosities appear to fall off more rapidly with increasing strain rate as distribution broadens.

Fig. 7 V_L/V_0 at the onset of draw resonance as a function of M_w/M_n .

Thus one may correlate the flow instabilities of linear polymers in elongational flow and the onset of draw resonance with the viscosity-shear rate behavior.

TUBULAR FILM EXTRUSION

Results

Two distinctive classes of processing instabilities have been observed in our tubular film experiments. Those are described in Fig. 8. At low blowup ratios the axisymmetric instability of Fig. 8a is observed. This tends to occur near a blowup ratio of 1.0. The range of occurrence of this behavior is shown in Fig. 9 where we display data in a drawdown ratio-blowup ratio plot for specific frostline heights. This type of representation of bubble stability is due to Kanai and White²³⁾ and was used by Minoshima and White¹⁸⁾. It can be seen that as blowup ratio increases, the bubble stabilizes and the instability moves to higher V_L/V_0 .

There is a second type of instability illustrated in Fig. 8b where the bubble moves in a helical manner. This type of instability occurs at high blowup ratios and low drawdown ratios. As blowup ratio increases the instability spreads to higher drawdown ratios. The area of this type instability increases with decreasing frost line height.

Fig. 8 Types of tubular film instabilities.

The polymers studied vary enormously in their bubble stability characteristics. The three LDPEs exhibit the most stable behavior. HDPE-3 and LLDPE-1 are unstable under almost all conditions. The behavior of HDPE-1 and HDPE-2 is intermediate.

Discussion

The general observations of this paper agree with those of earlier researchers. The detailed character of the helical instability seen here differs from that described by Kanai and White²³⁾ and Minoshima and White¹⁸⁾. The periodicity or wavelength of the helix is greatly changed. It would appear that the helical instability is associated with the air ring blowing onto the bubble. The screw extruder system we used had a different air ring design from that of the earlier investigations cited above.

The general observations comparing the responses of the different polyethylenes are similar. Kanai and White and Minoshima and White also noted the greater stability of the long chain branched LDPEs. They found that broadening molecular weight distribution had a stabilizing effect in tubular film extrusion unlike melt spinning.

Unlike the situation with melt spinning, there is not extensive literature on analysis of instabilities in tubular film extrusion. All experimental studies have been under non-isothermal conditions where temperature variations of rheological properties may dominate the inflation process. This certainly seems the case for bubble shape^{30,31)}. It is difficult to come up with a purely rheological argument for the ranges of stability diagrams of Fig. 9. However, the HDPEs and LLDPEs have very similar activation energies of viscous flow and the LDPEs have higher ones. More work is needed. Some speculation of mechanism is possible. At $BUR=1.0$, all materials show unstable behavior. Kanai and White²³⁾ showed that at constant throughput internal pressure decreases with BUR above $BUR=1.0$. Since at $BUR<1$ the pressure increases with BUR , there should be a maximum in internal pressure near $BUR=1$ which would cause unstable behavior.

ACKNOWLEDGMENT

This work was supported in part by the Division of Engineering of the National Science Foundation.

REFERENCES

- 1) Nason, H.K., *J. Appl. Phys.*, **16**, 338 (1945).
- 2) Spencer, R.S., and R.E. Dillon, *J. Colloid Sci.*, **4**, 241 (1949).
- 3) Tordella, J.P., *J. Appl. Phys.*, **27**, 454 (1956).
- 4) Tordella, J.P., *Rheol. Acta*, **1**, 216 (1958).
- 5) Howells, E.R., and J.J. Benbow, *Trans. Plastics Inst.*, **30**, 240 (1962).
- 6) Tordella, J.P., *J. Appl. Polym. Sci.*, **7**, 215 (1963).

Fig. 9 V_L/V_0 - R_L/R_0 plots of bubble stability.

(○ : stable, ▲ : axisymmetric instability)
(● : helical or bending instability)

- 7) Bialas, G.A., and J.L. White, *Rubber Chem. Technol.*, **42**, 675 (1969).
- 8) Oyanagi, Y., and Y. Yamaguchi, *J. Soc. Mat. Sci. Japan*, **20**, 659 (1971).
- 9) Vinogradov, G.V., N.I. Insarova, B.B. Boiko, and E.K. Borisenkova, *Polym. Eng. Sci.*, **12**, 323 (1979).
- 10) Freeman, H.I., and M.J. Coplan, *J. Appl. Polym. Sci.*, **8**, 2389 (1969).
- 11) Kase, S., *J. Appl. Polym. Sci.*, **18**, 3279 (1974).
- 12) White, J.L., and Y. Ide, *J. Appl. Polym. Sci.*, **22**, 3057 (1978).
- 13) Ghijsels, A., and J.J.S.M. Ente, "Rheology" Vol. 3, Applications edited by G. Astarita, G. Marrucci, and L. Nicolais, Plenum, NY (1980).

- 14) Minoshima, W., J.L. White, and J.E. Spruiell, *J. Appl. Polym. Sci.*, **25**, 287 (1980).
- 15) Yamane, H., and J.L. White, *Polym. Eng. Sci.*, **23**, 516 (1983).
- 16) Toriumi, K., A. Konda, and K. Fujimoto, *Seni Gakkaishi*, **41**, T-8 (1985).
- 17) White, J.L., and H. Yamane, *Pure Appl. Chem.*, **57**, 1441 (1985).
- 18) Minoshima, W., and J.L. White, *J. Non-Newt. Fluid Mech.* **19**, 275 (1986).
- 19) Kase, S., T. Matsuo, and Y. Yoshimoto, *Seni Kikai Gakkaishi*, **19**, 763 (1966).
- 20) Bergonzoni, A., and A.J. Di Cresci, *Polym. Eng. Sci.*, **6**, 45 (1966).
- 21) Han, C.D., and J.Y. Park, *J. Appl. Polym. Sci.*, **19**, 3241 (1975).
- 22) Han, C.D., and R. Shetty, *IEC Fund.*, **16**, 49 (1977).
- 23) Kanai, T., and J.L. White, *Polym. Eng. Sci.*, **24**, 1185 (1984).
- 24) White, J.L. and H. Yamane, *Pure Appl. Chem.*, (in press).
- 25) Yamane, H., and J.L. White, *Nihon Reoroji Gakkaishi*, **15**, 87 (1987).
- 26) White, J.L., *J. Appl. Polym. Sci.*, **9**, 2339 (1964).
- 27) Tordella, J.P., *Trans. Soc. Rheology*, **1**, 203 (1957).
- 28) Bagley, E.B., and A.M. Birks, *J. Appl. Phys.*, **31**, 556 (1960).
- 29) Ballenger, T.F., and J.L. White, *J. Appl. Polym. Sci.*, **15**, 1949 (1971).
- 30) Kanai, T., and J.L. White, *J. Polym. Eng.*, **5**, 135 (1985).
- 31) Yamane, H., and J.L. White, unpublished research.