

# Experimental Study of Elongational Flow and Failure of Polymer Melts

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## Synopsis

A new and simple instrument for measurement of elongational flow response of polymer melts in constant uniaxial extension rate experiments is described. Quantitative stress development data are presented for a series of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polystyrene (PS), polypropylene (PP), and poly(methyl methacrylate) (PMMA) melts. For small elongation rate  $E$ , linear viscoelastic behavior was observed; while for large  $E$ , LDPE and PS showed exponential stress growth, while HDPE and PP showed only linear stress growth. Stress relaxation experiments were carried out for several of the same melts in the instrument. Elongation to break and mechanisms of filament failure were studied. HDPE and PP have a tendency to neck and exhibit ductile failure, while at high  $E$ , LDPE and PS seem to show cohesive fracture. The elongational flow stress response data were compared to predictions of nonlinear viscoelastic fluid theory, specifically the Bogue-White formulation. The qualitative differences in responses of the melts studied were explained in terms of different dependences of the effective relaxation times on deformation rate and, more specifically, on values of the  $a$  parameter in the theory.

## INTRODUCTION

Industrial polymer fabrication operations have led through the years to considerable interest in the rheological characterization of polymer melts. Most studies have involved investigations of the stress response to shearing flows, and methods of investigation have become well established. Monographs<sup>1,2</sup> and review articles<sup>3</sup> describe the various shear flow measurements. The evaluation of shear stress and normal stress components which arise in such flows have been reported by numerous investigators. We give as examples two investigations from our own laboratories which possess extensive data, show the consistency of results from various instruments<sup>4,5</sup> and contain the evaluation of all three independent stress functions.<sup>5</sup>

In this paper, we consider the response of polymer melts in uniaxial elongational flow (Fig. 1) with constant elongation rate. Rheological characterization of materials such as pitch, tar-pitch blends, and shoemaker's wax in elongational flow was carried out in 1906 by Trouton who represented the response in terms of an elongational viscosity  $\chi$ . It was shown to be three times the shear viscosity  $\eta$ . Though there were some theoretical papers unpublished on elongational flow during the 1940s and 1950s,<sup>7-9</sup> it was not until the 1960s that experimental studies on polymer melts were carried out. Many of these papers were on the melt spinning of fibers<sup>10-18</sup> and related the local rate of elongation to the stress using an elongational viscosity  $\chi$ . This approach has been criticized because the polymer melts are viscoelastic and remember their deformation history. In the

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spinline, the elongation rate varies significantly with position.<sup>14,17,18</sup> Better defined elongational flow studies on polymer melts were initiated by Karam and Bellinger<sup>19</sup> and notably by Ballman<sup>20</sup> who carried out long-duration constant elongation rate experiments on polystyrene. In succeeding years, various investigators have studied this and other polymers in constant elongation rate and similar flows<sup>21-35</sup> (see Table I). Of special interest is the result of Meissner<sup>21,22,23</sup> on low-density polyethylene, which show a strain hardening stress buildup at high elongation rates. This has since been confirmed for other polymers.<sup>24-27</sup> The qualitative features of Meissner's results have been predicted from nonlinear viscoelastic fluid theory by Denn and Marrucci<sup>36</sup> and Chang and Lodge.<sup>37</sup> Reviews of elongational flow research have been given from differing viewpoints by Dealy,<sup>38</sup> Cogswell,<sup>33,34</sup> and the present authors.<sup>35</sup>

The problem of failure in elongational flow of polymer fluid filaments is of considerable practical as well as scientific interest. Nitschmann and Schrade<sup>8</sup> were among the first to consider this problem; and later, more detailed theoretical considerations were given by Ziabicki and Takserman-Krozer.<sup>39,40</sup> These early studies were in terms of fiber spinnability. More recently, isolated experimental

TABLE I  
Quantitative Experimental Studies of Isothermal Elongational Flow of Polymer Melts

Polymer	Investigator	Remarks
Low-density polyethylene	Meissner <sup>21,22,23</sup>	constant <i>E</i>
	Cogswell <sup>28,29,33</sup>	constant stress
	Chen et al. <sup>17</sup>	constant force
	Acierno et al. <sup>14</sup>	{ isothermal melt spinning
	Han and Lamonte <sup>15</sup>	
	Chen et al. <sup>17</sup>	
Polystyrene	Karam and Bellinger <sup>19</sup>	constant force
	Ballman <sup>20</sup>	constant <i>E</i>
	Everage and Ballman <sup>27</sup>	constant <i>E</i>
	Vinogradov et al. <sup>28</sup>	constant stress
	Munstedt <sup>31</sup>	constant stress
	Takaki and Bogue <sup>32</sup>	constant force
	Acierno et al. <sup>14</sup>	{ isothermal melt spinning
	Han and Lamonte <sup>15</sup>	
High-density polyethylene	Cogswell <sup>33</sup>	constant stress
	Han and Lamonte <sup>15</sup>	isothermal melt spinning
	Macosko and Lorntsen <sup>26</sup>	constant <i>E</i>
	[ Chen et al. <sup>17</sup> and Ide and White <sup>43</sup> report occurrence of necking in constant <i>E</i> and constant force experiments. ]	
	Cogswell <sup>33</sup>	constant stress
Polypropylene	Han and Lamonte <sup>15</sup>	{ isothermal melt spinning
	[ Cogswell <sup>33</sup> report problems of necking in constant stress experiments. ]	
	Cogswell <sup>33</sup>	constant stress
Poly(methyl methacrylate)	Vinogradov et al. <sup>24</sup>	constant <i>E</i>
Elastomers	Stevenson <sup>25</sup>	constant <i>E</i>
	Bankar et al. <sup>18</sup>	isothermal melt spinning

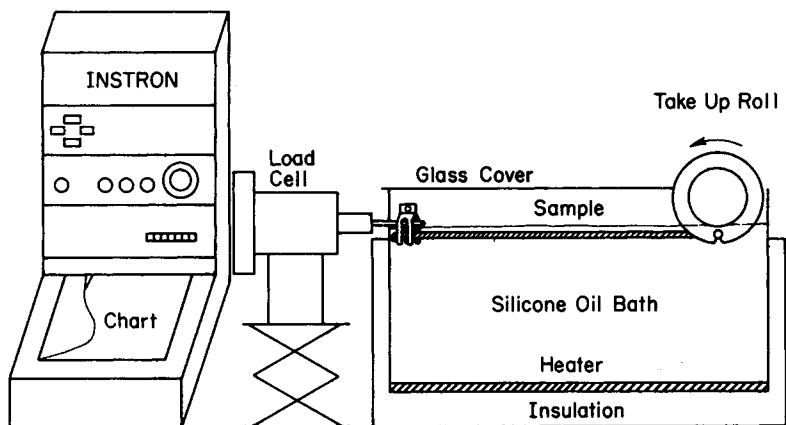


Fig. 1. Elongational flow apparatus.

observations on polymer melts have been reported by Cogswell<sup>33,34</sup> and the Tennessee group,<sup>14,17</sup> and an extensive study of narrow molecular weight distribution polystyrenes has been reported by Onogi and Kamei.<sup>41,42</sup> The present authors<sup>35,43,44</sup> have given a detailed theoretical analysis of the mechanisms of polymer fluid filament failure in constant elongation rate flows and presented a preliminary experimental study. Three mechanisms of filament failure in elongational flow have been distinguished: capillarity, ductile failure (necking), and cohesive fracture.

In this paper, we describe a new, simple experimental apparatus which allows the study of constant elongation rate stress response and failure of polymer melts. With this instrument, we investigate the stress response of several different polymer melts, including low-density polyethylenes (LDPE), high-density polyethylenes (HDPE), polystyrenes (PS), polypropylenes (PP), and poly(methyl methacrylate) (PMMA). Stress relaxation experiments are carried out on several of the same melts. The experimental results will be interpreted in terms of nonlinear viscoelastic fluid mechanics. Studies of the stress and elongation at failure as well as the mechanisms involved will be presented.

## EXPERIMENTAL

### Materials

A total of 14 different commercial plastics, including six low-density polyethylenes (LDPE), three high-density polyethylenes (HDPE), two polystyrenes (PS), two polypropylenes (PP), and one poly(methyl methacrylate) (PMMA) were included in this study. These polymers are summarized in Table II. Several of them have been rheologically characterized by various researchers in our laboratories. We summarize zero shear viscosities for the melts at the temperatures studied with reference to further information in Table II. Of these, two LDPE (1 and 3), two HDPE (1 and 2), two PS (1 and 2), two PP (1 and 2), and the PMMA were studied in the stress development experiments. Experiments were carried out at 160°C for LDPE, HDPE, and PS and at 180°C for PP and PMMA.

TABLE II  
 Polymer melts studied

Material	Commercial source	Designation in this paper	Rheological and molecular characterization	Zero shear viscosity $\times 10^{-3}$ , poise
Low-density polyethylene	Tennessee Eastman Tenite 800	LDPE-1	$MI = 1.7$ Ballenger et al. <sup>4</sup>	260 (160°C)  Chen and Bogue <sup>45,46</sup>
	Dow Tyon 560E	LDPE-2	$MI = 2.1$ Acierno et al. <sup>14</sup>	90 (160°C)
	Dow Tyon 610M	LDPE-3	$MI = 5.0$ White and Roman <sup>47</sup>	90 (180°C)
	Union Carbide DNA 0917	LDPE-4	$MI = 23$ Minagawa and White <sup>46</sup>	8 (180°C)
	Union Carbide DNDA 0455	LDPE-5	$MI = 60$	—
	Union Carbide DYDT	LDPE-6	polymer wax $MI > 2000$	—
High-density polyethylene	Phillips Marlex EMB 6001	HDPE-1	$MI = 0.1$ Minagawa and White <sup>48</sup>	2,000 (180°C)
	Tennessee Eastman Tenite 3340	HDPE-2	$MI = 2.6$ Ballenger et al. <sup>4</sup> Chen and Bogue <sup>45,46</sup>	165 (160°C)
	Phillips Marlex EMB 6050	HDPE-3	$MI = 5.0$ White and Roman <sup>47</sup>	75 (180°C)
Polystyrene	Shell TC3-30	PS-1	$M_w = 280 \times 10^3$ $M_w/M_n = 4.7$ Takaki and Bogue <sup>32</sup>	3100 (160°C)
	Dow Styron 678	PS-2	$M_w = 240 \times 10^3$ $M_w/M_n = 3.0$ White and Roman <sup>47</sup>	180 (180°C)
Polypropylene	Hercules Profax 6823	PP-1	$MI = 0.4$ $M_n = 4.3 \times 10^5$ Nadella et al. <sup>49</sup>	
	Hercules Profax 6423	PP-2	$MI = 6.6$ $M_n = 2.77 \times 10^5$ Nadella et al. <sup>49</sup>	
Poly(methyl methacrylate)	du Pont Lucite 147	PMMA	—	—

### Apparatus

A relatively simple apparatus for measuring elongational flow response of polymer melts was designed and constructed. It is shown in Figure 1. It consists of a constant-temperature silicone oil bath, an Instron tensile testing machine load cell, and a rotating roll attached to a motor with a speed controller. The polymer filament is stretched from the Instron load cell through the bath to the rotating roll around which it is wrapped. If the length of the filament is of length  $L$  and the roll of radius  $R$  rotates with angular velocity  $\Omega$  and linear roll velocity  $V$ , the elongation rate  $E$  is

$$E = dv_1/dx_1 = V/L = R\Omega/L. \quad (1)$$

The constant-temperature bath is controlled by a Hallikainen tube block heater

(Model 100) and a Variac within  $\pm 1^\circ\text{C}$ . The filament length between the clamps was 21.5 cm. The rotation speed of the take-up roll could be continuously varied giving a wide range of  $E$ . Two motors were used in the study: a  $\frac{1}{15}$  horsepower B and B motor with 12 rpm maximum allowed  $E$  of 0.005–0.2  $\text{sec}^{-1}$  with a 6.35-cm-diameter roll; and a Bodine Electric Company motor with 173 rpm maximum yielded  $E$  as high as 1.5  $\text{sec}^{-1}$  with a 3.18-cm-diameter roll. The motor speed was controlled by a B and B controller (Type ST-12).

### Procedure

The filaments were prepared by extrusion through an Instron capillary rheometer using a die of diameter 0.083 in. and  $L/D$  of 30. Different extrusion temperatures were used for the various polymers studied. The polymer filaments were wound up at low take-up velocities on a take-up roll and were later remelted in the hot silicone oil before beginning the experiment. The filaments exhibited shrinkage in the bath, were then removed, and their diameters measured. The filaments were then replaced in the bath and equilibrated before the beginning of the experiment. Density–temperature corrections to the cross-sectional area were made. These ranged from about 16% for HDPE and PP to 12% for LDPE and 5% for PS and PMMA. An estimate frictional drag on the filament was made using the theory of Batchelor.<sup>50</sup> There would seem to be 2% to 3% variation in tension along the filament for the lower viscosity filaments if we take the viscosity of the silicone oil to be 0.1 poise. This was neglected.

Stress relaxation experiments were carried out by stretching the filament 50–100% and allowing the stress to decay. A Type A 2000-gram Instron load cell attached to the console of the Instron table model tensile tester was used in these experiments. A 10-gram scale was used in the experiments. For PMMA and PS-1, a 100-gram full scale was used in some cases. The Instron load cell was calibrated in the same apparatus setup before use.

## RESULTS

### Stress Development

In Figure 2, we show tension (total force)  $F$  as a function of time, and in Figure 3, the elongation rate reduced stress development

$$\frac{F(E,t)}{A(t)E} = \frac{\sigma_{11}(E,t)}{E} = \chi(E,t) \quad (2)$$

for a low-density polyethylene LDPE-1 filament. Figure 4 contains stress development data for the LDPE-3 sample. In each case for small values of  $E$ ,  $\chi(E,t)$  increases to an asymptotic value close to  $3\eta_0$ , where  $\eta_0$  is the zero shear viscosity. At higher  $E$ ,  $\chi(E,t)$  increases in an unbounded manner.

Figures 5 and 6 show  $\chi(E,t)$  for HDPE-1 and HDPE-3. For small  $E$  the curves are qualitatively similar to the LDPE results. At higher  $E$ ,  $\chi(E,t)$  increases with time. However, the rate of increase is never as abrupt as the almost exponential character of the LDPE response. The magnitude of the stresses at failure is less.

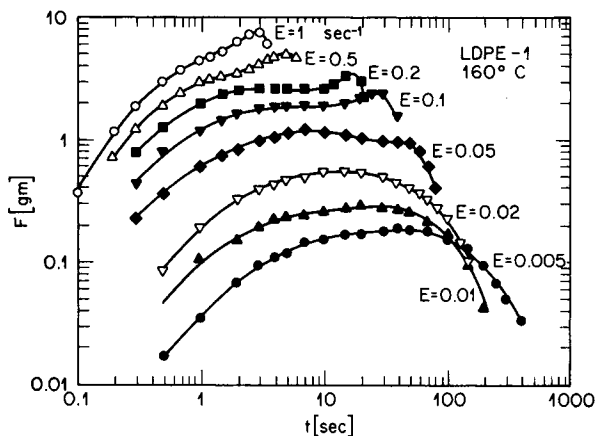


Fig. 2. Tension (force) vs time for LDPE-1.

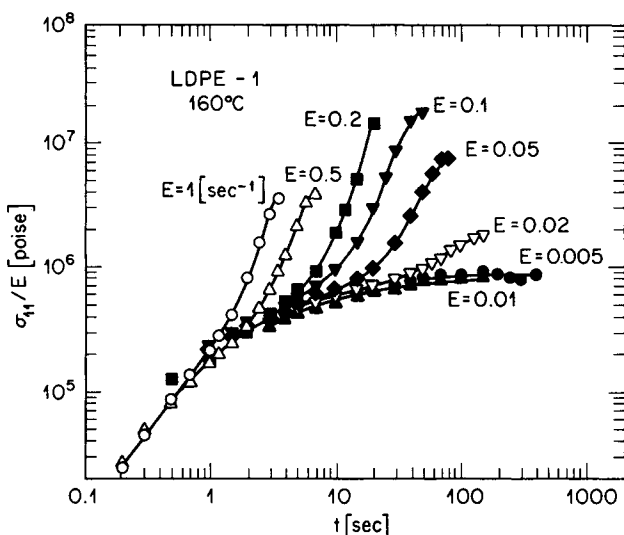


Fig. 3.  $\chi(E,t)$  vs time for LDPE-1 at various values of  $E$  at 160°C.

The results for the polystyrenes (PS) are summarized in Figures 7 and 8. At low  $E$ , the data increase asymptotically to a value of  $3\eta_0$ . At higher  $E$ ,  $\chi(E,t)$  increases in an unbounded manner and the data are similar to those of LDPE.

Figures 9 and 10 summarize  $\chi(E,t)$  data for polypropylenes PP-1 and PP-2. The data resemble the HDPE results. Figure 11 shows the  $\chi(E,t)$  function of poly(methyl methacrylate). This material proved difficult to work with because it absorbs moisture. The response appears to be generally similar to that of the polystyrenes.

An attempt was made to determine the reduced elongational viscosity  $\chi(E,\infty)/3\eta_0$  determined from the long-time asymptotic or maximum values of  $\chi(E,t)$  before failure and zero shear viscosity  $\eta_0$ . This is shown as a function of  $E$  in Figure 12 for the various melts studied. There are difficulties in constructing such a plot because at high  $E$ , failure occurs before a steady state is achieved. This is most obviously the case for the LDPE and PS samples; thus, all values for  $E > 0.02 \text{ sec}^{-1}$  are maxima. Figure 12 probably deserves only

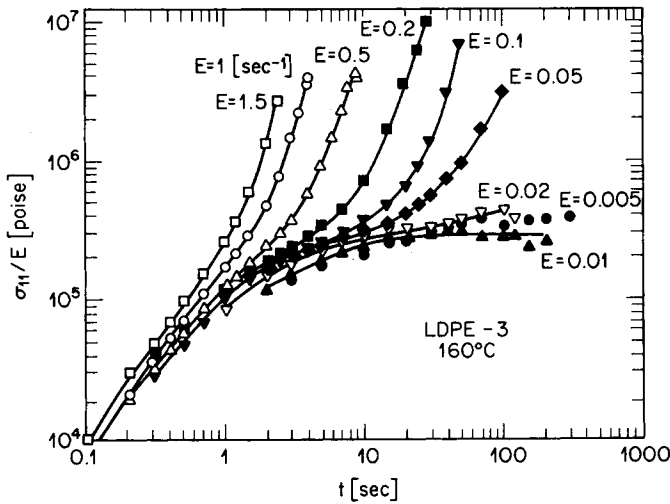


Fig. 4.  $\chi(E,t)$  vs time for LDPE-3 at 160°C.

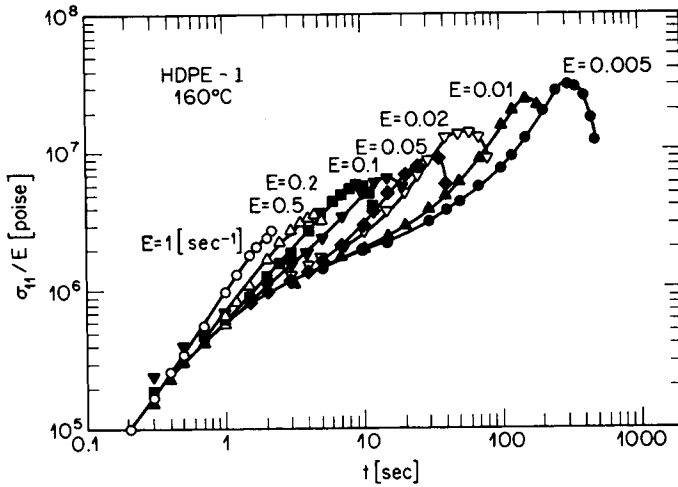


Fig. 5.  $\chi(E,t)$  vs time for HDPE-1 at 160°C.

qualitative interpretation;  $\chi(E, \infty)$  for the LDPEs rises rapidly from a value of  $3\eta_0$  at low  $E$ . The response of the PSs is similar, except the rise is less rapid. On the other hand, the HDPE and PP reduced data are lower. HDPE-1 and PP-1 show a  $\chi(E, \infty)$  decreasing with  $E$ .

### Stress Relaxation

The stress decay following extension for the melts was determined. We have interpreted these results in terms of standard stress relaxation experiments. For a tensile strain  $\gamma_0$ , we have

$$\sigma_{11}(t) = G(t)\gamma_0 \tag{3}$$

where  $G(t)$  is the shear relaxation modulus and  $\gamma_0$  is a suitable defined strain. For an infinitesimal stretch  $\Delta L$  of a sample of length  $L_0$ ,  $\gamma_0$  would be  $3\Delta L/L_0$ .

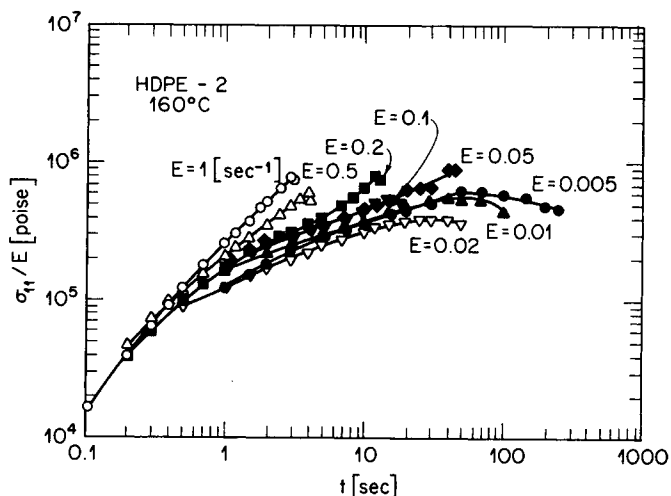


Fig. 6.  $\chi(E,t)$  vs time for HDPE-2 at 160°C.

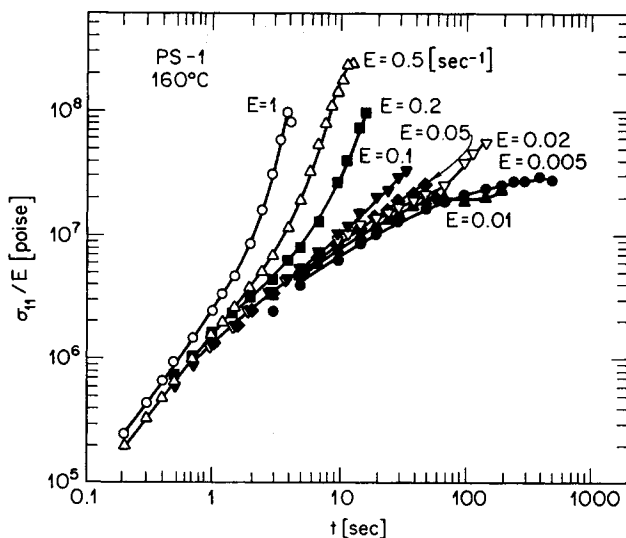


Fig. 7.  $\chi(E,t)$  vs time for PS-1 at 160°C.

However, we must use finite strains in this experiment. We have chosen to take  $\gamma_0$  to be the Finger strain measure which arises as a dominant term in viscoelastic fluid constitutive equations.<sup>2,3,14,17,43,51,52</sup> It follows that

$$\gamma_0 = \lambda^2 - \frac{1}{\lambda} = e^{2Et_0} - e^{-Et_0} \quad (4)$$

where  $\lambda$  is the extension ratio and  $t_0$  is the period of stretch.  $G(t)$  data have been traditionally represented as a series of exponentials<sup>52</sup>:



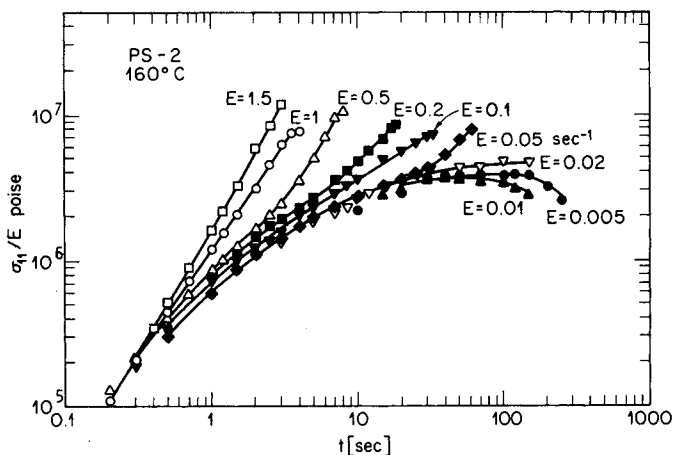


Fig. 8.  $\chi(E,t)$  vs time for PS-2 at 160°C.

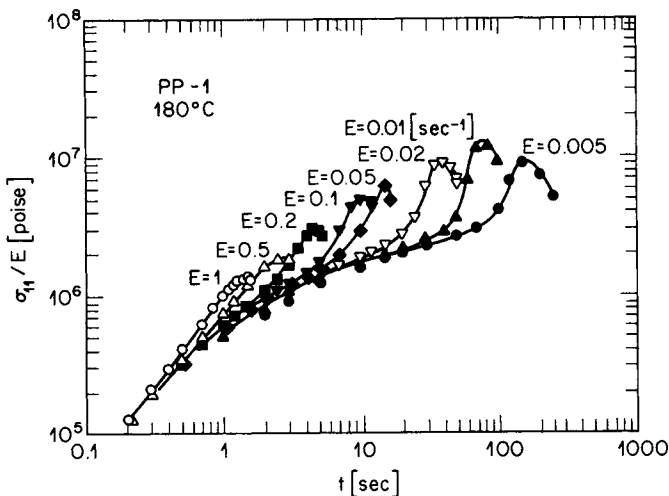


Fig. 9.  $\chi(E,t)$  vs time for PP-1 at 180°C.

$$G(t) = \sum_{i=1}^{i=m} G_i e^{-t/\tau_i} \tag{5}$$

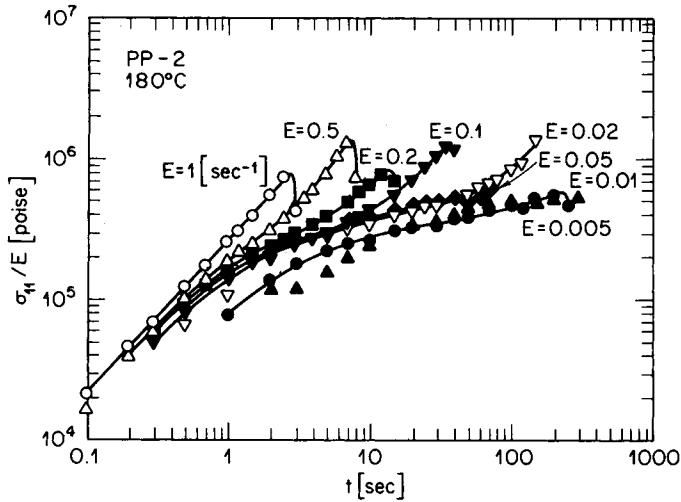
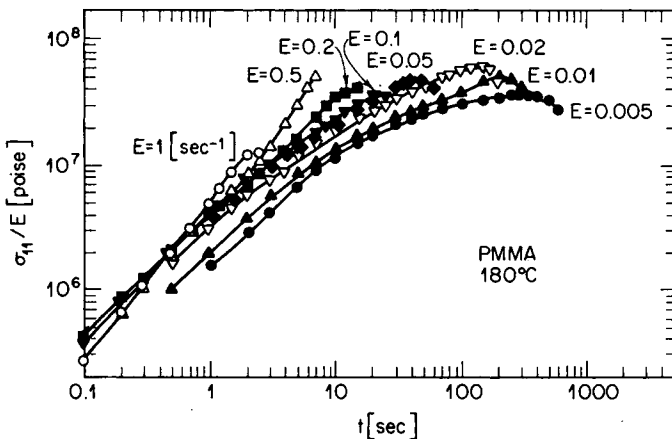
and Tobolsky and Murakami's "Procedure X"<sup>52,53,54</sup> has been used to determine the  $\tau_i$ . Specifically,  $\tau_m$  and  $G_m$  are determined from the slope and the intercept of the plot

$$\lim_{t \rightarrow \infty} \log \frac{\sigma_{11}(t)}{\gamma_0} = -\frac{t}{\tau_m} + \log G_m \tag{6a}$$

and  $G_{m-1}, \tau_{m-1}$  from

$$\lim_{t \rightarrow \infty} \log \left[ \frac{\sigma_{11}(t)}{\gamma_0} - G_m e^{-t/\tau_m} \right] = -\frac{t}{\tau_{m-1}} + \log G_{m-1} \tag{6b}$$

etc., where the distinction between natural and common logarithms must be considered. The results are summarized in Table IIIA.

Fig. 10.  $\chi(E,t)$  vs time for PP-2 at 180°C.Fig. 11.  $\chi(E,t)$  vs time for PMMA at 180°C.

### Mode of Failure

The low molecular weight LDPE melt filament LDPE-6 readily broke up in the silicone oil bath into drops because of capillarity. The LDPE-4 and LDPE-5 filaments can, on the other hand, be extended almost indefinitely. Indefinite elongation seems possible for LDPE-1, -2, and -3 as long as  $E$  is small. At high  $E$ , the filaments appear to fracture and exhibit "snap back." The variation in the critical extension ratio  $L(t_B)/L(0)$  is plotted as a function of  $E$  in Figure 13. Data obtained at 130°C are shown in Figure 13a and 160°C data, in Figure 13(b). Critical stresses at failure for the LDPE are around  $4 \times 10^6$  dynes/cm<sup>2</sup>.

The response for the HDPE is qualitatively different. The elongation ratios to break are considerably smaller and relatively independent of stretch rates. The mechanism of failure seems to involve necking, i.e., ductile failure. Critical  $L(t_B)/L(0)$  are plotted as a function of  $E$  in Figure 13(b).

The PS appear to fail by ductile failure at low  $E$  and by cohesive failure at large  $E$ . PMMA responds similarly.  $L(t_B)/L(0)$  is plotted versus  $E$  in Figure 14.

The PP behavior is similar to that of the HDPE and exhibits failure due to

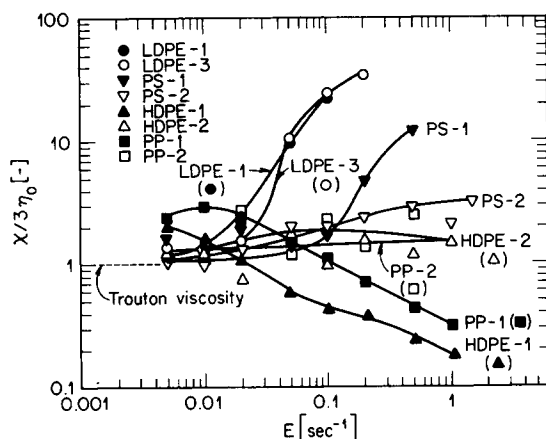


Fig. 12.  $\chi(E)$  for large  $t$  as a function of  $E$  for the various polymer melts investigated.

TABLE III  
Discrete Relaxation Spectra of Polymer Melts

	$m$	$m - 1$	$m - 2$	$m - 3$	$m - 4$	$m - 5$
A. Relaxation Experiment						
<i>LDPE-1</i> (160°C)						
$G_i$ , dynes/cm <sup>2</sup>	$1.35 \times 10^3$	$7.89 \times 10^3$	$2.60 \times 10^4$	$5.21 \times 10^4$		
$\tau_i$ , sec	82.6	13.5	2.60	0.789		
<i>HDPE-1</i> (160°C)						
$G_i$ , dynes/cm <sup>2</sup>	$6.10 \times 10^3$	$5.53 \times 10^3$	$1.36 \times 10^4$	$4.55 \times 10^4$	$1.10 \times 10^5$	$1.93 \times 10^5$
$\tau_i$ , sec	568	109	27.4	5.81	1.30	0.409
<i>PS-2</i> (160°C)						
$G_i$ , dynes/cm <sup>2</sup>	$3.14 \times 10^4$	$5.43 \times 10^4$	$1.41 \times 10^5$	$1.33 \times 10^5$		
$\tau_i$ , sec	23.2	4.09	1.14	0.434		
<i>PP-1</i> (180°C)						
$G_i$ , dynes/cm <sup>2</sup>	$4.40 \times 10^3$	$6.38 \times 10^3$	$1.18 \times 10^4$	$4.31 \times 10^5$	$1.98 \times 10^5$	
$\tau_i$ , sec	140	32.7	8.88	2.82	0.730	
B. Dynamic Experiment (Recalculated by Chen's <sup>44</sup> Continuous Spectrum)						
<i>LDPE-1</i> (160°C)						
$G_i$ , dynes/cm <sup>2</sup>	$4.19 \times 10^2$	$1.30 \times 10^4$	$6.54 \times 10^4$	$2.11 \times 10^5$	$5.35 \times 10^5$	$1.04 \times 10^6$
$\tau_i$ , sec	100	10	1	0.1	0.01	0.001
<i>HDPE-2</i> (160°C)						
$G_i$ , dynes/cm <sup>2</sup>	$6.20 \times 10^2$	$7.60 \times 10^3$	$4.37 \times 10^4$	$1.76 \times 10^5$	$7.48 \times 10^5$	$3.12 \times 10^6$
$\tau_i$ , sec	50	10	1	0.1	0.01	0.001

necking. The response is summarized in Figure 15. In the case of both the PP and HDPE, the necking behavior is more severe in the higher molecular weight melts PP-1 and HDPE-1.

## DISCUSSION

### Comparison with Earlier Experiments

The experimental stress buildup data for the LDPEs and PS are similar to experimental data previously published by earlier investigators. The LDPE results of Figures 3 and 4 resemble the LDPE data of Meissner,<sup>21,22</sup> and the PS results of Figures 7 and 8 resemble the data of Everage and Ballman.<sup>26</sup> However,

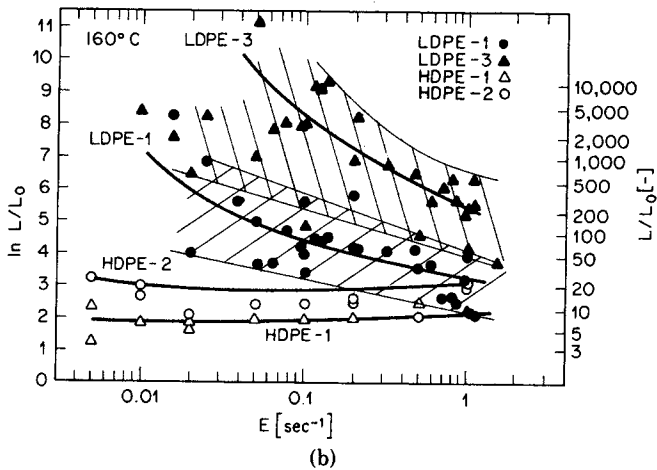
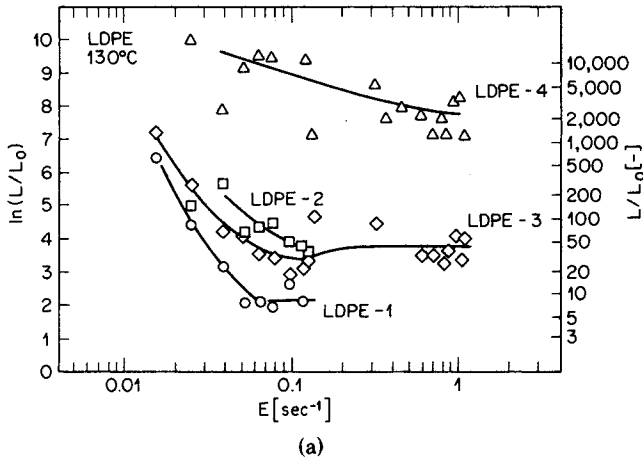


Fig. 13.  $L(t_B)/L(0)$  for (a) LDPE melts at 130°C, (b) HDPE and LDPE melts at 160°C.

our HDPE results differ from the data of Macosko and Lorntsen,<sup>25</sup> whose plots of  $\chi(E,t)$  resemble Meissner's LDPE experiments. The reason for this is not known, but different polymers were used and HDPEs with a wide range of properties are produced commercially.

Let us now turn to the filament stability results. The necking behavior of HDPE as opposed to stable behavior of LDPE was reported by Chen et al.<sup>17</sup> and Ide and White,<sup>43</sup> and a similar stable flow of commercial PS samples was indicated by Takaki and Bogue<sup>32</sup> who studied our sample PS-1. Cogswell<sup>33</sup> has reported necking in PP samples.

### Theoretical Interpretation of Stress Development

The nonlinear viscoelastic behavior of polymer melts has been represented by various researchers<sup>2,3,17,35,37,45,46,47,54,55</sup> using nonlinear constitutive equations of the form

$$\sigma = -pI + \int_0^\infty [m_1(z) \mathbf{c}^{-1} - m_2(z) \mathbf{c}] dz \quad (7)$$

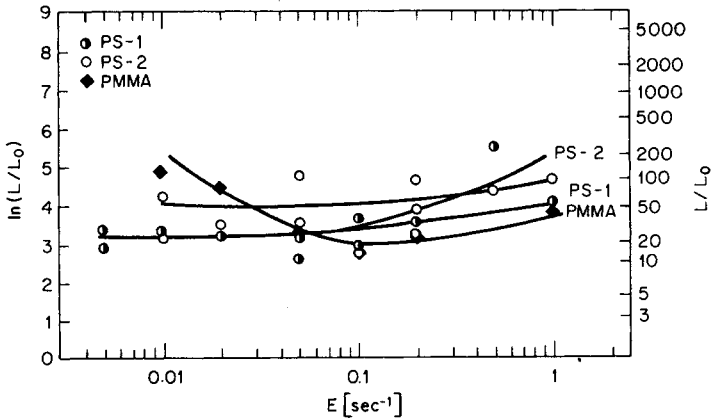


Fig. 14.  $L(t_B)/L(0)$  for PS (160°C) and PMMA (180°C) melts.

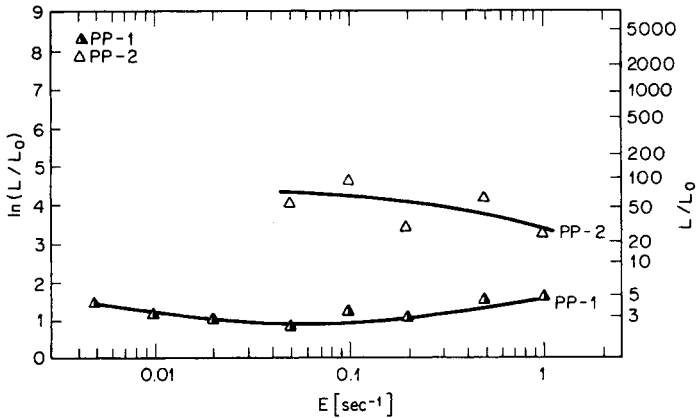


Fig. 15.  $L(t_B)/L(0)$  for PP melts at 180 °C.

where

$$m_1(z) = \left(1 + \frac{\epsilon}{2}\right) \bar{m}(z) \tag{8a}$$

$$m_2(z) = -\frac{\epsilon}{2} \bar{m}(z). \tag{8b}$$

Generally, we have found in our laboratories that reasonably good fits of experimental data are possible if we take

$$\bar{m}(z) = \sum_i \frac{G_i}{\tau_{ieff}} e^{-z/\tau_{ieff}} \tag{9a}$$

with  $\tau_{ieff}$  an effective relaxation time defined by

$$\tau_{ieff} = \frac{\tau_i}{1 + a\tau_i \bar{\Pi}_d^{1/2}} \tag{9b}$$

and

$$\bar{\Pi}_d^{1/2} = \frac{1}{z} \int_0^z \sqrt{2trd^2} ds \tag{9c}$$

In earlier studies, this equation has been successfully compared with stress responses in steady state and transient shear flow<sup>45,46,54</sup> and in elongational flows of melts where the deformation is induced by a falling weight.<sup>17,32</sup> The special case of eqs. (7)–(9) for which  $\epsilon$  and  $a$  are zero is the Lodge fluid.<sup>56,57</sup>

Consider a virgin polymer melt at time zero. We now subject the filament to constant elongation rate  $E$  stretching until time  $t$ . The predicted stress response is

$$\sigma_{11} = \int_0^\infty \{m_1(z) [c_{11}^{-1} - c_{22}^{-1}] - m_2(z) [c_{11} - c_{22}]\} dz \quad (10)$$

or

$$\begin{aligned} \sigma_{11} = & \left(1 + \frac{\epsilon}{2}\right) \sum_i G_i \left\{ \frac{1 + \sqrt{3a\tau_i E}}{1 - (2 - \sqrt{3a})\tau_i E} (1 - \exp^{-\{[1 - (2 - \sqrt{3a})\tau_i E]t/\tau_i\}}) \right. \\ & - \frac{1 + \sqrt{3a\tau_i E}}{1 + (1 + \sqrt{3a})\tau_i E} (1 - \exp^{-[1 + (1 + \sqrt{3a})\tau_i E]t/\tau_i}) \\ & + [\exp^{-t/\tau_i} + \sqrt{3aEtEi}(t/\tau_i)](\exp^{[2 - \sqrt{3a}]Et} - \exp^{-(1 - \sqrt{3a})Et}) \left. \right\} \\ & - \frac{\epsilon}{2} \sum_i G_i \left\{ \frac{1 + \sqrt{3a\tau_i E}}{1 - (1 - \sqrt{3a})\tau_i E} [1 - \exp^{-[1 - (1 - \sqrt{3a})\tau_i E]t/\tau_i}] \right. \\ & - \frac{1 + \sqrt{3a\tau_i E}}{1 + (2 + \sqrt{3a})\tau_i E} (1 - \exp^{-[1 + (2 + \sqrt{3a})\tau_i E]t/\tau_i}) \\ & + [\exp^{-t/\tau_i} + \sqrt{3aEtEi}(t/\tau_i)](\exp^{(1 - \sqrt{3a})Et} - \exp^{-(2 + \sqrt{3a})Et}) \left. \right\} \quad (11) \end{aligned}$$

where

$$Ei(x) = \int_x^\infty \frac{e^{-x}}{x} dx.$$

The term in  $m_1(z)$  is dominant especially for small  $\epsilon$ . The value of  $a$  plays an important role. The derivation leading to eq. (11) is similar to that given by Denn and Marrucci<sup>36</sup> and Chang and Lodge<sup>37</sup> for simpler viscoelastic fluid models.

In order to contrast eq. (11) with experiment, we need to possess values of  $\tau_i$ ,  $G_i$ ,  $\epsilon$ , and  $a$  for the melts studied. For LDPE-1 and HDPE-2, extensive studies of dynamic properties have been carried out by Chen and Bogue.<sup>45,46</sup> These have been converted to discrete spectra and are summarized in Table IIIB. Our stress relaxation measurements have been interpreted in terms of  $G_i$  and  $\tau_i$ , and these are also summarized in Table III. The appropriate value of  $a$  has been studied for LDPE-1, HDPE-2, and a polystyrene melt by Chen and Bogue. Slightly different values were obtained from viscosity and normal stress data, with the latter generally being higher. For the LDPE-1 at 160°C,  $a$  would seem in the range of 0.2 to 0.5, while for HDPE-2, it would be 0.4 to 0.8. From the results of Lee and White<sup>5</sup> on similar polymer melts,  $\epsilon/2$  should be small and negative and in the range of 0 to -0.4.

In Figures 16, 17, and 18, we have plotted our  $\sigma_{11}(E, t)$  data for three melts studied together with theoretical  $\sigma_{11}(E, t)$  based upon eq. (11) (at  $E = 0.01, 0.1$ , and  $1.0 \text{ sec}^{-1}$ ) for various values of  $a$  and with  $\epsilon$  set equal to zero. We omit comparisons for deformation times less than 1 sec where questions of transients

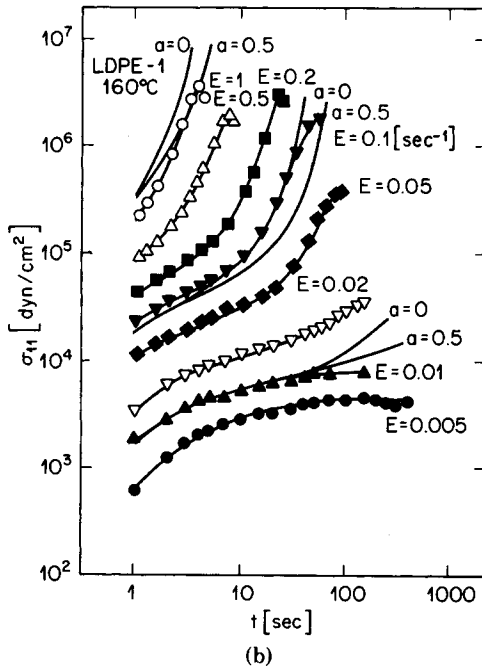
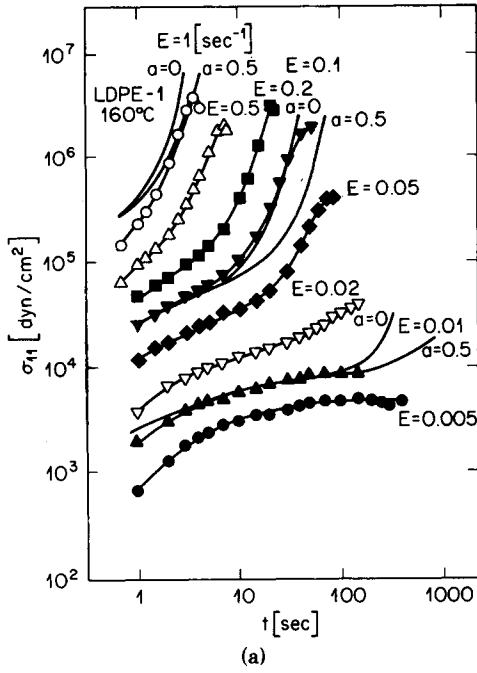


Fig. 16. Theoretical and experimental stress buildup data for LDPE-1 (a) based on dynamic data, (b) based on stress relaxation data.

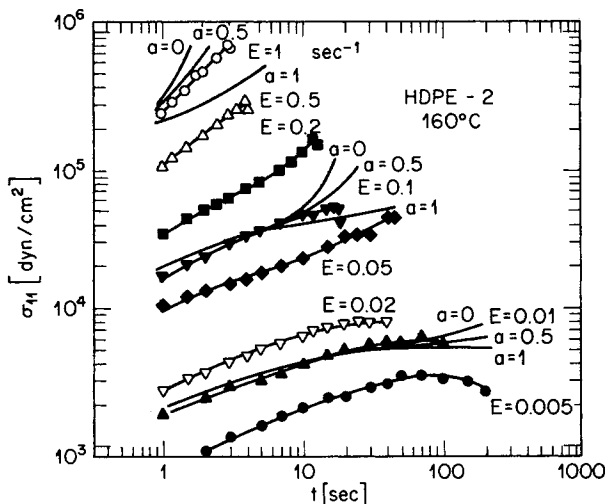


Fig. 17. Theoretical and experimental stress buildup data for HDPE-2 (based on dynamic data).

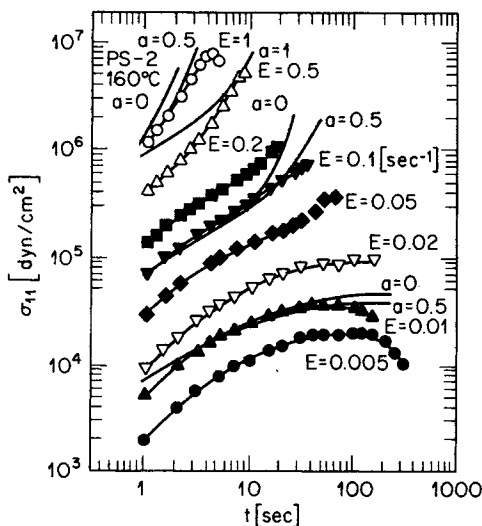


Fig. 18. Theoretical and experimental stress buildup for PS-2 (based on stress relaxation data).

may be raised. The  $a = 0$  curves correspond to a Lodge fluid. Depending upon the value of  $a$ , the agreement can be good. It may be seen that LDPE-1 corresponds to  $a$  values between 0 and 0.5. The appropriate value of  $a$  for the PS-2 is somewhat larger. HDPE-2 exhibits lower stress buildup, and the data are best fit with larger  $a$  values in the range of 0.5–1.0.

The exponential stress buildup in the LDPE and PS samples is similar to the Chang-Lodge calculation for  $a = 0$  and our own small  $a$  computations. The near-linear stress buildup of the HDPE and PP is typical of predictions of larger  $a$  values.

The long-duration flow elongational viscosity for the model of eqs. (9)–(11) is given by (with  $\epsilon = 0$ )

$$\chi = \chi(E, \infty) = \sum_i \frac{3G_i \tau_{ieff}}{(1 - 2E\tau_{ieff})(1 + E\tau_{ieff})} \quad (12)$$



At high values of  $E$ ,  $\chi$  becomes unbounded. This is determined by the criterion

$$E_{\text{crit}} = \frac{1}{2\tau_{\text{meff}}} \quad (13)$$

where  $\tau_{\text{meff}}$  is given by eq. (9b), i.e.,

$$\tau_{\text{meff}} = \frac{\tau_m}{1 + \sqrt{3}(a\tau_mE)}. \quad (14)$$

This allows us to write the unbounded  $\chi$  criterion as

$$E_{\text{crit}} = \frac{1}{2\tau_m} \left( \frac{1}{1 - (\sqrt{3}/2)a} \right). \quad (15)$$

As  $a$  becomes larger,  $E_{\text{crit}}$  increases; and when  $a$  exceeds  $2/\sqrt{3}$  or 1.16,  $E_{\text{crit}}$  becomes infinite. This should help make clear the significance of the higher values of  $a$  for the HDPE in elongational flow experiments. It decreases the tendency to unbounded stress growth.

### Interpretation of Filament Failure

We cannot fail to notice that the mode of failure, elongation to break, and apparent tensile strengths of the filaments correlate with  $\chi(E,t)$  data. Cohesive failure, large tensile strengths, and large elongations to break are associated with rapid exponential  $\chi-t$  data and  $\chi$  increasing with  $E$ . There is a clear trend among the polymer melts with an ordering

$$\text{LDPE} > \text{PS} > \text{HDPE} \sim \text{PP}.$$

According to our theoretical analysis, this corresponds also to the apparent ordering of the  $a$  values and the relative deformation rate dependence of the  $\tau_{\text{ieff}}$ .

Analyses of the growth of defects in viscoelastic fluid filaments during elongational flow have been given variously by the authors<sup>35,43</sup> and by Chang and Lodge.<sup>58</sup> We will show in a later paper that it is possible to generalize these approaches to represent the different filament stability behavior of the above polymers during elongational flow.\*

### CONCLUSIONS

1. Experimental studies of stress development in uniaxial flow with constant elongation rate have been carried out for four polyethylenes (two low-density type LDPEs and two high-density type HDPEs), two polystyrenes (PS), two polypropylenes (PP), and a poly(methyl methacrylate).

2. Stress relaxation measurements have been carried out with many of the same melts. These are interpreted in terms of discrete relaxation spectra.

3. At low elongation rates, all polymers show near-linear viscoelastic behavior. At higher rates, the LDPE and PS show unbounded exponential stress growth and the HDPE and PP, only linear stress growth.

4. Nonlinear viscoelastic fluid constitutive equations of the Bogue-White type

\* Note added in proof. This paper has since been published [Ide and White *J. Non-Newtonian Fluid Mech.*, 2, 281 (1977)].

are able to fit the experimental data for stress buildup if the  $a$  parameter in the theory orders

$$a_{LDPE} < a_{PS} < a_{PP} \sim a_{HDPE} \quad (16)$$

where  $a_{LDPE}$  is about 0.3 and  $a_{HDPE}$  between 0.5 and 1.0.

5. Studies of filament failure have been carried out on several LDPE, HDPE, PS, PP, and a PMMA samples. These show that LDPEs fail by cohesive fracture and the HDPEs and PRs by ductile failure (necking), especially in high molecular weight materials. PS appears to show ductile failure at low rates and cohesive fracture at high rates.

6. Low molecular weight LDPEs extend indefinitely, especially at low rates. The elongation to break of LDPEs decrease with increasing elongation rate. The HDPEs and PPs show much smaller elongations to break, especially the higher molecular weight polymers. Generally, for HDPE and PP, the elongation to break is independent of elongation rate.

7. The rate of stress buildup and  $a$  parameter correlate with mechanism and elongation to break.

It should be said finally that the results of this paper are consistent with those of earlier investigators.

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