

# Flow Properties of Various Irradiated Resins of PTFE (Teflon)\*

W. KEITH FISHER<sup>†</sup> and J. C. CORELLI, *Department of Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York 12181*

## Synopsis

Changes in the melt viscosity of PTFE exposed to various radiation doses in air were measured using a capillary rheometer. The melt viscosity decreases dramatically after exposure to 2.5 MRad, but between 2.5 and 5 MRad there is an increase in viscosity which is attributed to the formation of branches and crosslinks. Above 5 MRad, the melt viscosity decreases with dose. Plots of log apparent melt viscosity vs. log apparent shear rate are given for PTFE exposed to various radiation doses. The data in each of these plots can be fit by a straight line (power law), and changes in the slopes of these lines are interpreted to indicate changes in the molecular weight distribution. It is postulated that the observed decrease in the slopes of these lines after irradiation is caused by a narrowing of the molecular weight distribution because of the decrease in the number of molecules at the high molecular weight end of the distribution. The melt viscosity of a PTFE sample irradiated to a given dose was less for a sample of low preirradiation crystallinity than for an otherwise identical sample of higher crystallinity. This crystallinity dependence of viscosity is related to differences in oxygen diffusion properties of crystalline and amorphous PTFE.

## INTRODUCTION

In a previous communication,<sup>1</sup> we described in detail ionizing radiation-induced changes in the chemical structure, the crystalline content, and the structure, and also in less detail the changes in the flow properties of poly(tetrafluoroethylene) (PTFE). The purpose of this report is to present further results and details on changes in the melt flow properties of PTFE upon exposure to ionizing radiation.

It is well known that exposure to ionizing radiation causes a dramatic decrease in the melt viscosity of PTFE due to main chain scission. The slope of the melt viscosity-vs.-shear rate curve yields qualitative information on the radiation-induced changes in the molecular weight distribution. Also, the amount of swelling and general appearance of the polymer extrudate as it leaves the viscosimeter capillary gives information on the deviation from purely viscous Newtonian flow behavior.

\* Based on the Ph.D. thesis of W. Keith Fisher at Rensselaer Polytechnic Institute, May 1981.

<sup>†</sup> Present address: Monsanto Plastics and Resins Co., Bloomfield Technical Center, 101 Granby St., Bloomfield, CT 06002.

## EXPERIMENTAL

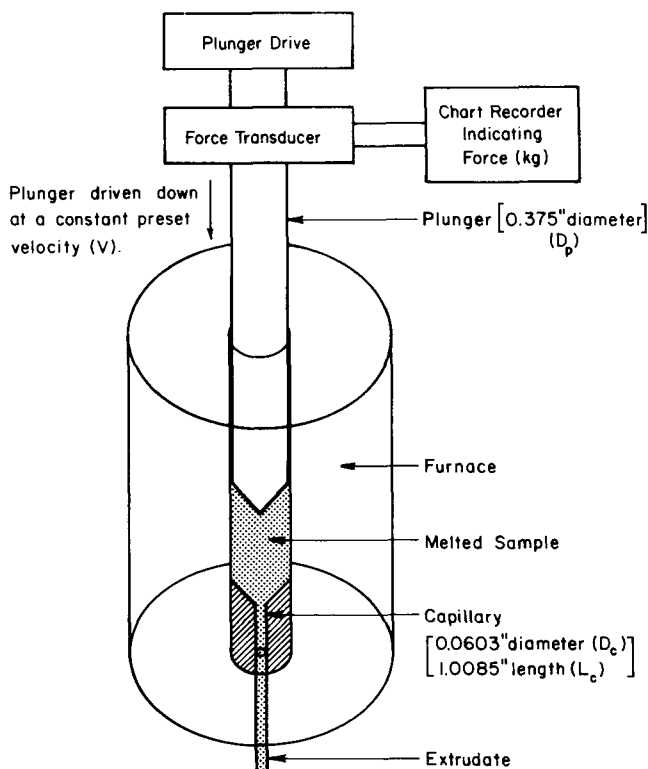
### Sample Material and Radiation Equipment

The PTFE sample material used in this work consists of DuPont Teflon Resins 6, 6C, and 7A. The approximate number-average molecular weights of these resins are<sup>2</sup> Resin 6: 2 to  $5 \times 10^6$  dalton; Resin 7A: 50 to  $500 \times 10^6$  daltons. Resin 6C is a modified PTFE homopolymer with a number-average molecular weight intermediate between Resin 6 and 7A.

The radiation source used was a 0.5–0.8 MeV resonant transformer cathode ray accelerator built by the General Electric Company.<sup>3</sup> The details of the method of irradiating the sample are given elsewhere<sup>1</sup> and will not be repeated here.

### Melt Viscosity

The changes in melt viscosity induced in PTFE by ionizing radiation were measured using an Instron model 3211 constant-shear capillary rheometer system. The model 3211 consists of a heated barrel with a capillary at one end (Fig. 1). The capillary used in this work was 0.1532 cm in diameter and 2.516 cm in length. The sample was packed into the cylinder and left to melt for 20 min prior to measurement. The material was then forced through the capillary at a con-



$$\dot{\gamma}_a (\text{sec}^{-1}) = \frac{2}{15} \frac{D_p^2}{D_c^3} V = 33.64 V (\text{cm/min})$$

$$\text{Shear Stress} = \frac{980655}{\pi D_p^2} \frac{D_c}{L_c} (\text{Force}) = 20,577 \cdot \text{Force (kg)}$$

Fig. 1. Schematic diagram of the Instron capillary rheometer.

stant shear rate using a plunger connected to a force transducer. The force necessary to push the material through the capillary at the constant shear rate was measured, and from this measurement the shear stress at the capillary wall can be easily calculated. Knowing the shear stress and the shear rate, the viscosity can be calculated (shear stress/shear rate). Viscosity measurements were made at 335, 350, and 380°C.

## RESULTS AND DISCUSSION

In general, non-Newtonian and viscoelastic behavior are characteristic of polymer melt flow. The purely viscous flow of an ideal Newtonian fluid involves no recoverable deformation, just the relative motion of successive layers of fluid past each other at fixed velocities as long as a shearing force is applied. For an ideal Newtonian fluid, the shear stress  $\tau$  is directly proportional to the time rate of change of shear strain (shear rate  $\dot{\gamma}$ ):

$$\tau = \eta \dot{\gamma} \quad (1)$$

The proportionality constant  $\eta$  is the Newtonian viscosity. Low-molecular-weight gases and liquids exhibit ideal Newtonian flow behavior.

At the other extreme, a material may exhibit completely reversible deformation in response to an applied shearing stress. This is called elastic deformation. Upon application of a shearing stress to an elastic body, that body will deform instantly; and, if the stress is removed, it will return essentially instantaneously to its initial shape and size. For an ideal elastic body, the shear stress  $\tau$  is directly proportional to the magnitude of the shear strain  $\gamma$ :

$$\tau = G \gamma \quad (2)$$

where the constant  $G$  is the shear modulus.

Flow properties of polymer melts are between those of an ideally elastic and an ideally viscous material and exhibit what is known as viscoelastic flow characteristics. For polymer melts, the following equation relates the shear stress  $\tau$  to the shear rate  $\dot{\gamma}$ :

$$\tau = \eta(\dot{\gamma}) \dot{\gamma} \quad (3)$$

Unlike the case of a Newtonian fluid where the viscosity is constant, here the viscosity is a function of the shear rate  $\eta(\dot{\gamma})$ . Thus, it is necessary to measure the viscosity over a wide range of shear rates to characterize the flow properties of a viscoelastic fluid.

In many cases, the dependence of viscosity on shear rate over a wide range of shear rates may be expressed in a simple mathematical form called the power law, which is given by the equation

$$\eta = \eta_0 \left[ \frac{\dot{\gamma}}{\dot{\gamma}_0} \right]^{n-1} \quad (4)$$

where the subscripted quantities refer to a reference state. For most polymer melts  $n < 1$ , so that the viscosity decreases with increasing shear rate. This sort of behavior is called "shear thinning" and is characteristic of the melt flow of irradiated PTFE. Newtonian flow is characterized by  $n = 1$ . As  $n$  becomes smaller, the shear thinning deviation from ideal Newtonian flow becomes greater.

TABLE I  
Flow Index Values Using the Power Law Equation (4) with  $\dot{\gamma}_0 = 1 \text{ s}^{-1}$

Sample	$n - 1$	$n$	Correlation coefficient
Resin 7A, 2.5 MRad	-0.764	0.236	0.996
Resin 7A, 5 MRad	-0.905	0.095	0.999
Resin 7A, 10 MRad	-0.450	0.550	0.999
Resin 7A, 25 MRad	-0.400	0.600	1.000
Resin 6C, 2.5 MRad	-0.749	0.251	0.997
Resin 6C, 5 MRad	-0.866	0.134	0.994
Resin 6C, 10 MRad	-0.501	0.499	0.994
Resin 6C, 25 MRad	-0.456	0.544	0.998
Resin 6, 2.5 MRad	-0.796	0.204	0.993
Resin 6, 5 MRad	-0.832	0.168	0.999
Resin 6, 10 MRad	-0.481	0.519	0.998
Resin 6, 25 MRad	-0.519	0.481	0.997

Thus,  $n$  may be considered as a measure of the non-Newtonian character of a polymer melt and is often known as the "flow index" of a material. Some flow index values were calculated and are presented in Table I for various samples of irradiated PTFE.

Qualitatively, the cause of the decrease in viscosity with increasing shear rate has to do with the length and flexibility of macromolecules. Because of the length of polymer chains, the molecules tend to become entangled. These entanglements are not permanent chemical bonds (i.e., not crosslinks) but merely molecules which are looped about one another so that they will have some freedom to move relative to each other. At low shear rates, the molecular entanglements remain intact because of the low velocity gradient in the polymer stream. Thus, with the application of a shearing stress, the molecules are unable to move independently of one another, but the movement of one molecule causes an adjacent molecule to be dragged along with it.

This coordinated motion causes the viscosity to be higher at low shear rates. At higher shear rates (high shear stresses), the molecules begin to become untangled and are able to orient themselves in the direction of flow. Because of the reduction in the number of entanglements, the molecules are able to slide by each other more easily so that the viscosity of the polymer melt is lowered. Bueche<sup>4</sup> has developed a theory to calculate melt viscosities considering chain entanglement.

The  $n$  values listed in Table I were obtained from linear least-squares fits to the data plotted in Figures 2 through 5. These figures show plots of the log of the apparent viscosity ( $\log \eta_a$ ) vs. the log of the apparent shear rate ( $\log \dot{\gamma}_a$ ). The apparent shear rate is the shear rate of a Newtonian fluid extruded under the same conditions as the actual polymer melt and is given by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (5)$$

where  $Q$  is the volumetric flow rate of the melt and  $R$  is the capillary radius.

The apparent viscosity is given by

$$\eta_a = \frac{\tau}{\dot{\gamma}_a} \quad (6)$$

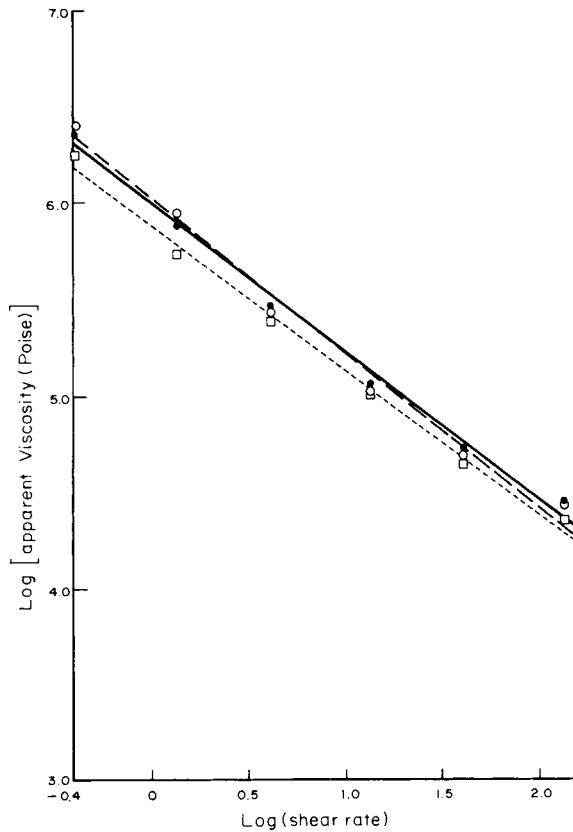
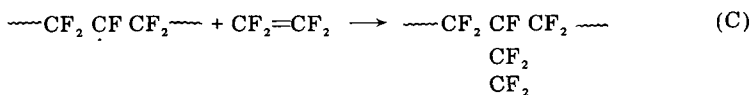
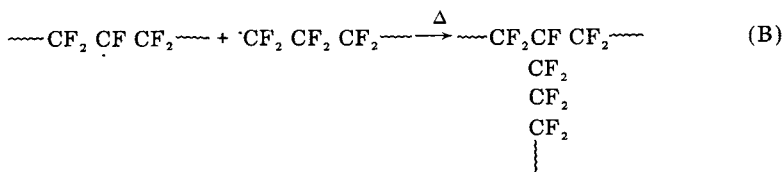
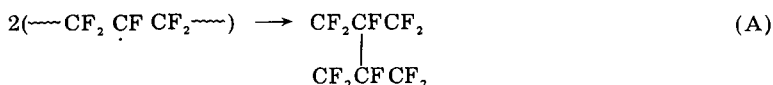


Fig. 2. Log apparent melt viscosity vs. log apparent shear rate measured at 350°C for samples of PTFE Resins 7A (●), 6 (○), and 6C (□) irradiated to 2.5 MRads in air.

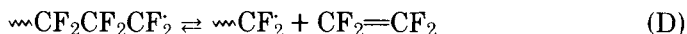
The apparent shear rate is only an approximation to the actual shear rate, but it is common practice for melt viscosity data to be presented in the form of a plot of apparent viscosity vs. apparent shear rate. It can be seen by examining Table I that for the PTFE resins (Resins 7A, 6, and 6C) the value of  $n$  decreases between 2.5 and 5 MRad and then increases dramatically between 5 and 10 MRads. This large increase in the  $n$  value indicates that the polymer melt is behaving more like an ideal Newtonian fluid. Also, Figures 6 through 8, which are plots of  $\log \eta_a$  vs.  $\log \dot{\gamma}_a$  for three different PTFE resins, show a large drop in apparent melt viscosity between 5 and 10 MRad. There is also a large drop in melt viscosity between 0 and 2.5 MRad because the viscosity of unirradiated PTFE is approximately  $10^{11}$  poise at 380°C.<sup>5</sup>

The tendency toward Newtonian flow and the drop in viscosity can be explained in terms of radiation-induced chain scission which results in a lowering of the molecular weight. Shorter molecules will have fewer entanglements per molecule so that they will be able to flow past one another more easily, thus resulting in a lowering of the viscosity after irradiation of the polymer material. The increase in the  $n$  value is also caused by the reduction in entanglement density upon exposure to radiation. The fewer entanglements present, the more the polymer molecules will be independent of each other and will therefore exhibit flow properties closer to those of a Newtonian fluid (where there is no physical connection between molecules).

The net decrease in viscosity with radiation dose for PTFE indicates that main chain scission is dominant when the irradiation is carried out in air. The increases in the  $n$  value and also the increase in viscosity between 2.5 and 5 MRad for the PTFE resins at low shear rates (Figs. 6 through 8) indicate that there may be some other reactions that occur upon exposure to radiation which result in an increase in the number of molecules at the high end of the molecular weight distribution. Reactions which would accomplish this are the crosslinking reaction (reaction A) and branching or grafting reactions (reactions B and C):



The crosslinking reaction (reaction A) is highly unlikely for reasons of steric hindrance.<sup>6</sup> Reaction B, which involves the combination of two long polymer chain fragments, is possible but probably only occurs at elevated temperatures where there is greater chain mobility. The grafting experiments of Bro et al.<sup>7</sup> and also the thermodynamic analysis of Bryant<sup>8</sup> have shown the validity of reaction C. Tetrafluoroethylene monomer may be produced upon exposure to ionizing radiation via the following reaction:



The double arrows on reaction D indicate that much of the monomer almost immediately repolymerizes but some may remain to be consumed via reaction C. The chain branches produced in reaction C may lead to some degree of crosslinking if the propagating branch chain is terminated via recombination with a secondary free radical on a neighboring polymer chain.

The radiation-induced decrease in melt viscosity is some 10- to 100- fold less when the irradiation is carried out in an inert atmosphere or vacuum.<sup>9</sup> Under these conditions, there is no oxygen available to react with the radiation-induced free radicals so that recombination, branching, and crosslinking reactions become more important relative to the number of chain scissions. It has previously been shown, by infrared analysis, that fewer end groups are formed when PTFE is irradiated under vacuum than when irradiated in air.<sup>1</sup> The infrared absorption band corresponding to the acid fluoride end group does not appear, but the ab-

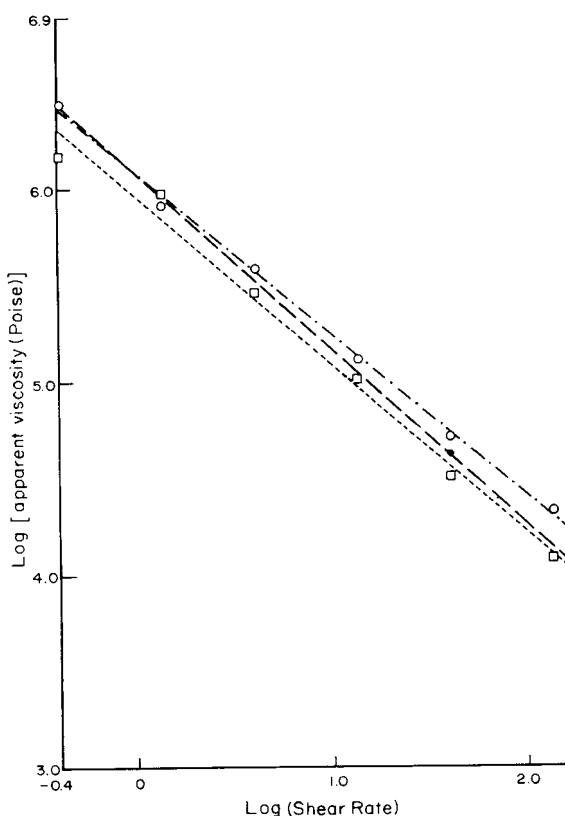


Fig. 3. Log apparent melt viscosity vs. log apparent shear rate measured at 350°C for samples of PTFE Resins 7A (●), 6 (○), and 6C (□) irradiated to 5 MRads in air.

sorption bands corresponding to branching or crosslinking come in more strongly than if the irradiation was done in the presence of oxygen.

Generally, an increase in the  $n$  value for a polymer melt indicates not only that the flow properties are closer to those of a Newtonian fluid but also a narrowing of the molecular weight distribution. It is postulated that the increase in  $n$  values with increasing dose for PTFE is caused by a narrowing of the molecular weight distribution because of a reduction in the number of polymer molecules at the high end of the molecular weight distribution. The higher-molecular-weight molecules, because of their large physical size, will suffer more chain scissions per molecule than low-molecular-weight molecules so that the number of molecules at the high end of the molecular weight distribution will be reduced. It is these long, high-molecular-weight molecules that would have the most entanglements and would be largely responsible for deviations from Newtonian flow behavior.

For a polydisperse system, the number-average molecular weight is given by

$$\bar{M}_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} \quad (7)$$

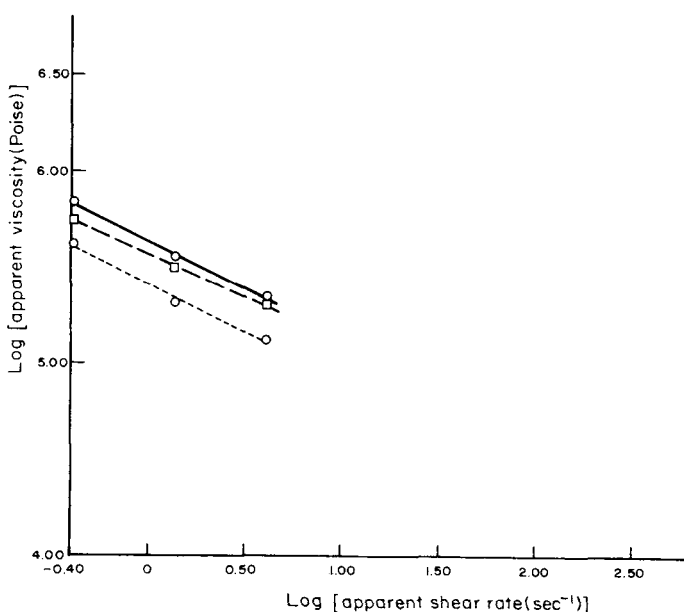


Fig. 4. Log apparent melt viscosity vs. log apparent shear rate measured at 350°C for samples of PTFE Resins 7A (--□--), 6 (—○—), and 6C (---○---) irradiated to 10 MRads in air.

and the weight-average molecular weight is given by

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \quad (8)$$

where  $N_i$  is the number of molecules of molecular weight  $M_i$  in a sample of known mass. The polydispersity is the ratio of the weight-average to the number-average molecular weight and is a measure of the width of the molecular weight distribution:

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \frac{\sum_{i=1}^{\infty} N_i}{\sum_{i=1}^{\infty} N_i M_i} \quad (9)$$

The polydispersity is always greater than 1, except for a monodisperse system, where it equals 1. To show that the preferential scissioning of the high-molecular-weight chains results in a narrowing of the molecular weight distribution (reduction in the polydispersity), two cases are considered: (1) chain scissioning is independent of molecular weight, and (2) chain scissioning depends on the molecular weight to the first order.<sup>10</sup>

For case 1, the total number of chain scissions occurring in all polymer molecules of molecular weight  $M_i$  is

$$n_i = K_1 N_i \quad (10)$$



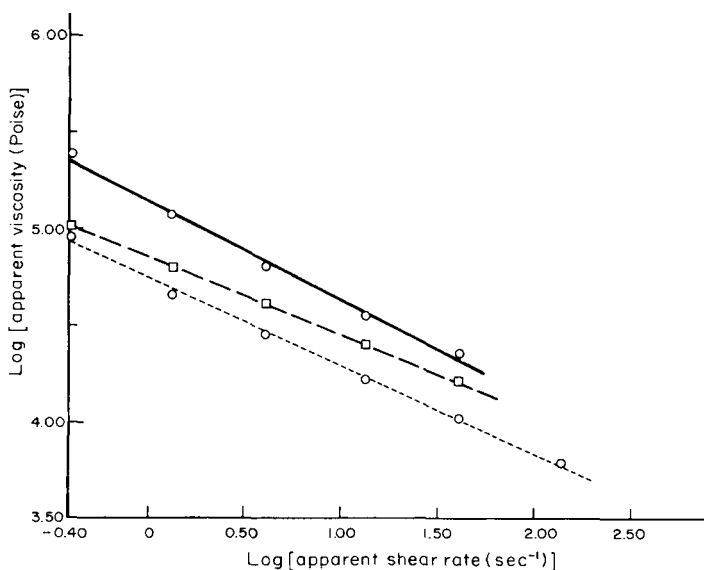


Fig. 5. Log apparent melt viscosity vs. log apparent shear rate measured at 350°C for samples of PTFE Resins 7A (--□--), 6 (—○—), and 6C (---○---) irradiated in 25 MRads.

where  $n_i$  is the total number of chain scissions,  $N_i$  is the number of molecules of molecular weight  $M_i$  in a sample of known mass, and  $K_1$  is a constant. The molecular weight after radiation-induced chain scissioning of all molecules with initial molecular weight  $M_i$  is

$$m_i = \frac{M_i}{K_1} \quad (11)$$

Substituting eqs. (10) and (11) into eqs. (7) and (8) yields

$$\bar{M}_n = \frac{\sum_{i=1}^{\infty} (n_i/K_1)K_1m_i}{\sum_{i=1}^{\infty} (n_i/K_1)} = \frac{K_1 \sum_{i=1}^{\infty} n_i m_i}{\sum_{i=1}^{\infty} n_i} \quad (12)$$

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} (n_i/K_1)(K_1m_i)^2}{\sum_{i=1}^{\infty} (n_i/K_1)K_1m_i} = \frac{K_1 \sum_{i=1}^{\infty} n_i m_i^2}{\sum_{i=1}^{\infty} n_i m_i} \quad (13)$$

The final, postirradiation polydispersity becomes

$$\left. \frac{\bar{M}_w}{\bar{M}_n} \right|_{\text{final}} = \frac{\sum_{i=1}^{\infty} n_i m_i^2}{\sum_{i=1}^{\infty} n_i m_i} \frac{\sum_{i=1}^{\infty} n_i}{\sum_{i=1}^{\infty} n_i m_i} = \left. \frac{\bar{M}_w}{\bar{M}_n} \right|_{\text{initial}} \quad (14)$$

Because one sums over all molecular weight fractions, eq. (14) indicates that the polydispersity does not change when chain scission is independent of molecular weight.

For case 2, the following relations are true:

$$n_i = (K_2 M_i) N_i \quad (15)$$

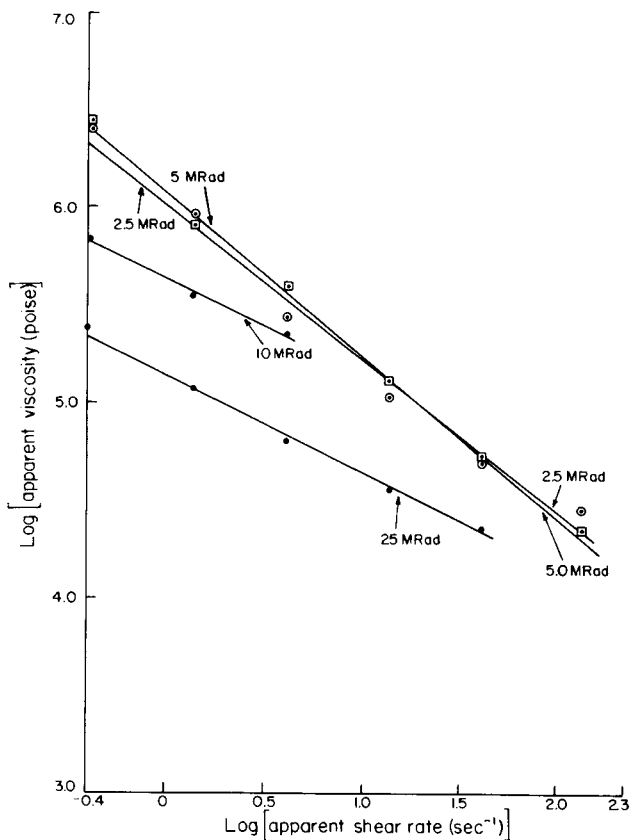


Fig. 6. Log apparent melt viscosity vs. log apparent shear rate measured at 350°C for PTFE Resin 6 irradiated in air to doses shown: (○) 2.5 MRad; (□) 5.0 MRad.

and

$$m_i = \frac{M_i}{K_2 M_i} = \frac{1}{K_2} \quad (16)$$

where  $K_2$  is a constant.

Equation (15) says that the number of chain scissions ( $n_i$ ) occurring in all polymer molecules of molecular weight  $M_i$  depends upon  $M_i$  to the first order. Substituting eqs. (15) and (16) into eqs. (7) and (8) yields

$$\bar{M}_n = \frac{\sum_{i=1}^{\infty} (n_i/K_2 M_i)(1/K_2)}{\sum_{i=1}^{\infty} (n_i/K_2 M_i)} = \frac{1}{K_2} \quad (17)$$

and

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} (n_i/K_2 M_i)(1/K_2)^2}{\sum_{i=1}^{\infty} (n_i/K_2 M_i)(1/K_2)} = \frac{1}{K_2} \quad (18)$$

The polydispersity now becomes

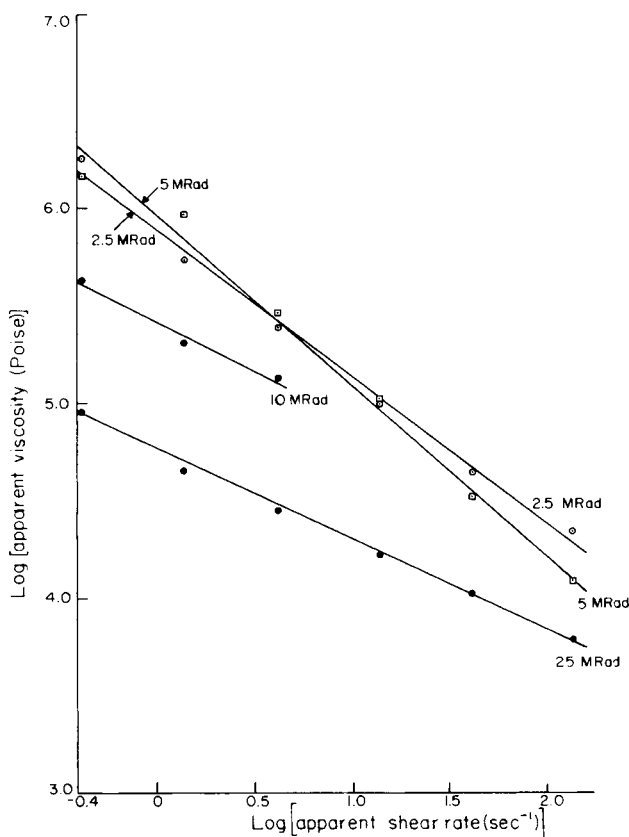


Fig. 7. Log apparent melt viscosity vs. log apparent shear rate at 350°C for PTFE Resin 6C irradiated in air to doses shown: (○) 2.5 MRad; (□) 5 MRad; (●) 10, 25 MRad.

$$\left. \frac{\overline{M}_w}{\overline{M}_n} \right|_{\text{final}} = 1 \quad (19)$$

This shows that when the number of chain scissions per molecule in a polymer fraction of molecular weight  $M_i$  depends on  $M_i$ , polydispersity narrows dramatically from its initial value down to that corresponding to a monodisperse distribution.

The data in Table I indicate qualitatively that there is narrowing of the molecular weight distribution because  $n$  increases with dose. Thus, there would seem to be some dependence of the number of chain scissions per molecule on the molecular weight of that molecule. The dependence of the number of chain scissions per molecule on the molecular weight lies somewhere between cases 1 and 2.

Physically, the dependence of the number of chain scissions per polymer molecule ( $n_i/N_i$ ) of molecular weight fraction  $M_i$  on  $M_i$  may be explained in terms of the size of the molecule. The higher-molecular-weight molecules are larger than the molecules of lower molecular weight and therefore, assuming the radiation-induced free radicals are created uniformly throughout the polymer matrix, would undergo more chain scissions.

In Figure 9 are shown photographic enlargements of the extrudate of PTFE Resin 6 irradiated to 2.5 and 5 MRads as it emerged from the capillary at ap-

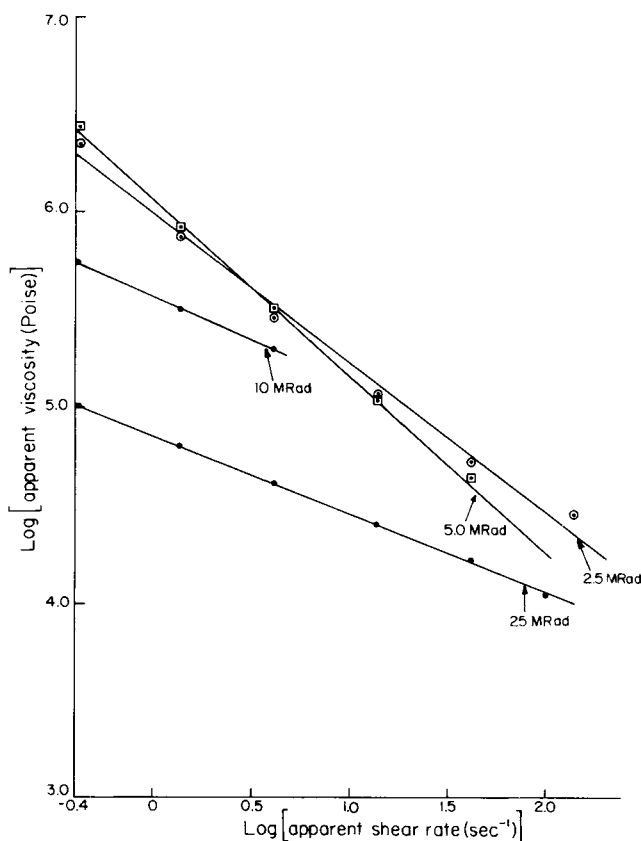
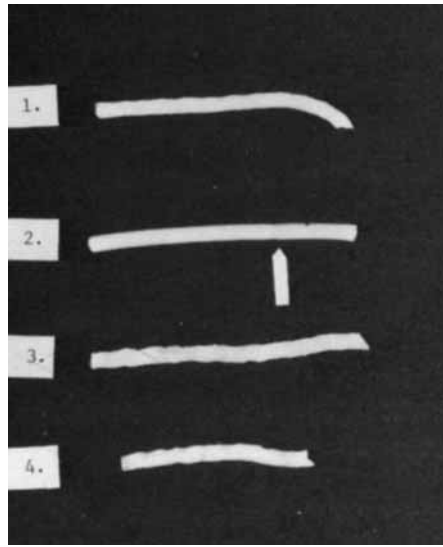


Fig. 8. Log apparent melt viscosity vs. log apparent shear rate for PTFE Resin 7A irradiated in air to doses shown: (○) 2.5 MRad; (□) 5.5 MRad; (●) 10, 25 MRad.

parent shear rates of  $0.404$  and  $13.46 \text{ s}^{-1}$ . Also indicated are the die swell measurements. The 2.5-MRad extrudate at  $\dot{\gamma}_a = 0.404 \text{ s}^{-1}$  shows slight surface irregularity in the form of ripples. The 5-MRad extrudate at  $\dot{\gamma}_a = 0.404 \text{ s}^{-1}$  is characteristic of the type of extrudate produced by severe stick-slip behavior. The portion of extrudate to the left of the arrow exhibits a very fine surface roughness and corresponds to the condition in which the polymer melt was slipping through the capillary at a higher shear rate than the low shear rate portion of the extrudate to the right of the arrow. The smooth low shear rate portion of the extrudate, instead of emerging from the capillary in a straight thread, tended to become twisted as it cooled. This effect is shown in Figure 10. Again, during the extrusion of the sample shown in Figure 10, stick-slip behavior was observed. Referring again to Figure 9, the higher-shear-rate extrudate shows a more severe melt fracture than the lower-shear-rate extrudate. The 2.5-MRad sample exhibits surface ripples, and the 5-MRad sample shows some screw dislocation behavior.

Figure 11 shows extrudate samples of PTFE Resin 7A irradiated to 2.5 and 5 MRads and extruded at shear rates of  $4.04$  and  $13.46 \text{ cm}^{-1}$ . At  $\dot{\gamma}_a = 4.04 \text{ s}^{-1}$ , the 2.5-MRad samples indicate some surface ripples. The 5-MRad extrudate is very smooth but somewhat twisted. At  $\dot{\gamma}_a = 13.46 \text{ s}^{-1}$ , the 2.5-MRad extrudate again shows surface ripples, and the 5-MRad sample exhibits screw dislocations.



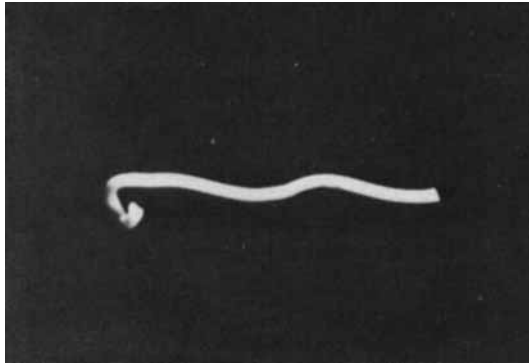
Resin 6		
	Dose (MRad)	Die Swell
Apparent Shear Rate = 0.404 sec <sup>-1</sup>		
1.	2.5	0.93
2.	5	0.98
Apparent Shear Rate = 13.46 sec <sup>-1</sup>		
3.	2.5	0.98
4.	5	1.02
Capillary Temperature = 350°C		

Fig. 9. Extrudate samples of PTFE Resin 6.

Figure 12 shows a sample of the extrudate of PTFE Resin 7A irradiated to 5 MRad and extruded at a shear rate of 2.02 s<sup>-1</sup>. A high degree of screw dislocation behavior is apparent. In all the samples of Figures 9 and 11, the die swell increases in going from 2.5 to 5.0 MRad.

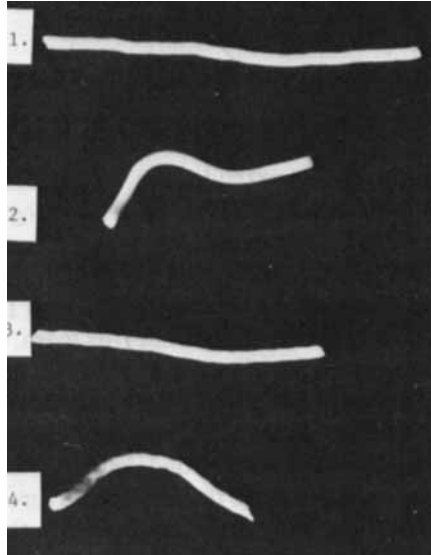
Samples of PTFE measured at shear rates of 40.37 and 134.6 s<sup>-1</sup> showed severe melt fracture at all dose levels investigated in this work.

In general, the deviating shapes of polymer extrudates have been attributed to elastic failure of response of the viscoelastic polymer melts on being forced through a capillary.<sup>11</sup> The deviation in the shape of the extrudate thread begins after a certain critical shear stress is exceeded, usually about  $2 \times 10^6$  dyn/cm<sup>2</sup>.<sup>12</sup> Birefringence studies have shown that the first departure from smooth laminar flow for melt-processible fluoropolymers occurs within the capillary. Presumably, this first departure from smooth laminar flow results in the ripple type of surface roughness observed in the PTFE extrudates mentioned above. At a somewhat higher shear stress, stick-slip behavior occurs at the capillary wall. Examples of this type of extrudate behavior are shown in Figures 9 and 11. Ultimately, rupture or fracture of the elastically deformed flowing polymer stream occurs at the capillary entrance. Differential elastic recovery caused by the fracture phenomena within a capillary or at its entrance results in distorted emerging streams, the magnitude of which increases with increasing shear rate.<sup>13,14</sup>



Teflon<sup>®</sup> Resin 6  
 Apparent Shear Rate =  $1.35 \text{ sec}^{-1}$   
 Dose = 5 MRads  
 Die Swell = 0.95  
 Capillary Temperature =  $350^{\circ}\text{C}$

Fig. 10. Example of twisted extrudate.

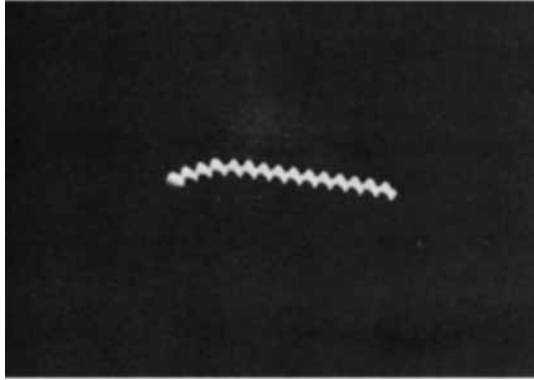


Resin 7A

	Dose (MRad)	Die Swell
Apparent Shear Rate = $4.04 \text{ sec}^{-1}$		
1.	2.5	0.95
2.	5.	1.01
Apparent Shear Rate = $13.46 \text{ sec}^{-1}$		
3.	2.5	0.96
4.	5	1.02

Capillary Temperature =  $350^{\circ}\text{C}$

Fig. 11. Extrudate samples of PTFE Resin 7A.



Teflon<sup>®</sup> Resin 7A  
 Apparent Shear Rate =  $2.02 \text{ sec}^{-1}$   
 Dose = 5 MRad  
 Die Swell = 1.18  
 Capillary Temperature =  $380^\circ\text{C}$

Fig. 12. Example of an extrudate exhibiting screw dislocations.

Figure 13 shows the effect of capillary temperature on the apparent melt viscosity of PTFE Resin 7A irradiated to 25 MRads. Also shown in this figure are plots of log apparent viscosity ( $\eta_a$ ) vs. log apparent shear rate ( $\dot{\gamma}_a$ ) for PTFE

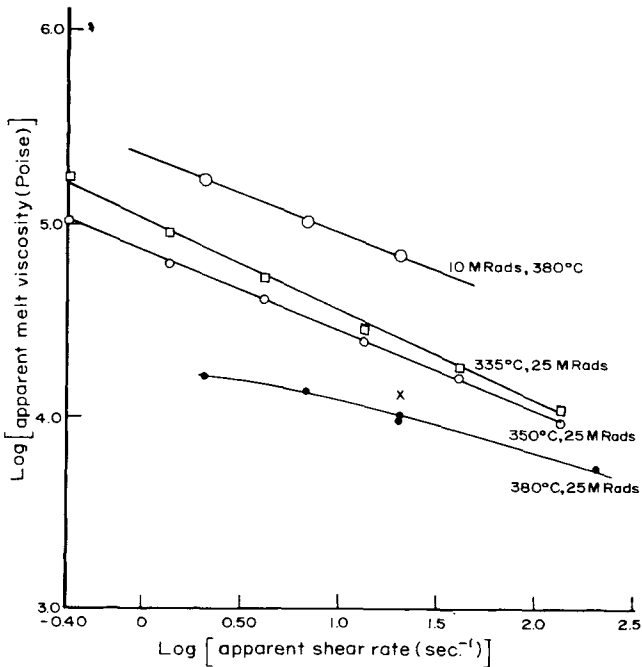


Fig. 13. Log apparent melt viscosity vs. log apparent shear rate for PTFE Resin 7A irradiated to 25 MRads in air taken at capillary temperatures of 335, 350, and  $380^\circ\text{C}$ . Also shown are data for 10-MRad dose with  $380^\circ\text{C}$  capillary temperature: (x) PTFE Resin 6, 25 MRad  $380^\circ\text{C}$ .

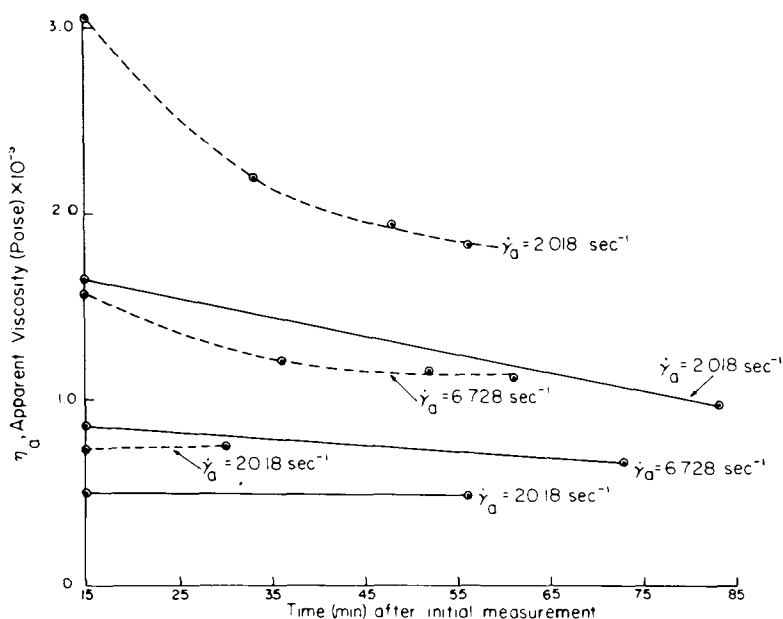


Fig. 14. Effect of storage time in the rheometer barrel at 380°C and differences in preirradiation crystallinity in the postirradiation melt viscosity for PTFE Resin 6: (---) 10.8 MRad, slow cool; (—) 10.8 MRad, water quench.

Resin 7A irradiated to doses of 10 and 25 MRad and measured at a capillary temperature of 380°C. The log apparent viscosity of PTFE Resin 6 irradiated to a dose of 25 MRads and measured at a capillary temperature of 380°C is also plotted on Figure 13 at an apparent shear rate of 20.2 s<sup>-1</sup>. As expected, the viscosity decreases as the capillary temperature increases at all shear rates measured. There is a large decrease in viscosity between 10 and 25 MRad when the viscosity is measured at 380°C and, as stated earlier, can be attributed to radiation-induced chain scissions resulting in a lowering of the molecular weight.

Only one datum point for Resin 6 was obtained (see Fig. 13) because of a large number of bubbles in the polymer melt, which made the acquisition of reliable data very difficult. This problem of bubble formation in the polymer melt stream was particularly severe at doses greater than 10 MRad. Viscosity measurements were attempted for PTFE irradiated to 50 MRad; but, because of the formation of a large number of bubbles in the polymer melt, consistent data could not be obtained. These bubbles are caused by pyrolysis within the viscosimeter barrel of the irradiated polymer. The number of bubbles formed increases with increasing radiation dose. The bubbles consist of CO<sub>2</sub>, CF<sub>2</sub>O, and C<sub>2</sub>F<sub>6</sub> gases as determined by infrared analysis.<sup>15</sup>

Finally, Figure 14 shows the effect of differing preirradiation crystallinity on the apparent viscosity of PTFE Resin 6 irradiated to 10.8 MRad. Before irradiation, the sample material was melted and held at 380°C for 15 min. Some of the material was cooled from the melt very slowly (yielding a more crystalline sample), while the rest of the material was quenched from 380°C in cold water (yielding a sample of lower crystallinity). The slow-cooled sample had a density of 2.26 g/cc, while the density of the quenched sample was 2.13 g/cc. As can be



seen from Figure 14, the sample of higher crystallinity had a higher viscosity at each of the three shear rates measured. Also, the effect of storage time in the rheometer barrel at 380°C on viscosity is shown.

The lower viscosity for the sample of lower crystallinity can be explained by realizing that most of the chain scission reactions in PTFE involve oxygen.<sup>1</sup> In the sample of low crystallinity, a greater amount of polymer material is able to react with oxygen. Oxygen molecules are unable to diffuse into the tightly packed crystalline phase so that oxygen-related scission reactions will not occur in the crystalline phase. Thus, because more material is available to react with oxygen in the sample of low crystallinity, more chain scission reactions will occur in this sample, resulting in a lower molecular weight than in the highly crystalline material. A lower molecular weight means a lower viscosity, and this is what is observed (Fig. 14). This result correlates well with the observed increase in the number of oxygen-related end groups with decreasing sample crystallinity as shown by the infrared spectroscopy results of Ref. 1.

Plotted in Figure 14 is the apparent viscosity vs. storage time at 380°C in the rheometer capillary. The decrease in viscosity with storage time can be explained by two mechanisms. First, storage at high temperature may cause residual unreacted free radicals to react causing further chain scissions. Second, after storage at 380°C for extended periods of time, some thermal degradation occurs. Some of the sample material which had been stored the longest began to show discoloration (turning from white to a yellow-brown hue) indicative of thermal degradation.

## SUMMARY AND CONCLUSIONS

In summary, we conclude that exposure of PTFE to ionizing radiation causes a decrease in viscosity due to chain scission. There is a slight increase in viscosity between 2.5 and 5 MRads for PTFE Resins 6, 6C, and 7A, which we conclude is caused by branching and crosslinking reactions in the crystalline region of the polymer. The flow index values increase at doses greater than 5 MRads, indicating that the flow properties are closer to those of a Newtonian fluid. It is concluded that the approach to Newtonian flow properties is caused chiefly by a reduction in the number of molecules at the high end of the molecular weight distribution. Departure from purely viscous flow is shown by the deviating shapes of the PTFE extrudate, and we conclude that this is caused by radiation-induced chain branching and crosslinking reactions and also chain entanglements. Inasmuch as the viscosity of a sample of PTFE irradiated to a given dose depends on its preirradiation crystalline content, a sample of low crystallinity will yield a lower viscosity than a high-crystallinity sample irradiated to the same dose.

The authors thank Radiation Dynamics, Inc., for financial support of most of this research. Special thanks are given to Prof. C. I. Chung of the Materials Engineering Department and Prof. J. A. Moore of the Chemistry Department at Rensselaer Polytechnic Institute for discussions on key questions of this research. Resins 6 and 7A were kindly supplied by Du Pont Chemical Co. through Dr. C. Sperati, who also supplied valuable information. The authors also thank Mr. Allen Fenwick of Instron Corp. for use of his capillary rheometer for measurements at 350 and 380°C. Finally, the excellent typing of the manuscript by Marilyn Namone is gratefully acknowledged by the authors.

### References

1. W. K. Fisher and J. C. Corelli, *J. Polym. Sci. Polym. Chem.*, **19**, 2465 (1981).
2. Dr. Carlton Sperati, Ohio University, Department of Chemical Engineering, private communication.
3. W. F. Westendorp, *Radiation Sources*, ed. by A. Charlesby, McMillan, New York, 1964, p. 171.
4. F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).
5. J. A. Blair, Fluorocarbons, Polymers, in *Encyclopedia of Industrial Chemical Analysis*, Vol. 13, 1971, p. 80.
6. R. E. Florin, L. A. Wall, and D. W. Brown, *J. Res. Natl. Bur. Stand.*, **644**, 269 (1960).
7. M. I. Bro, E. R. Lovejoy, and G. R. McKay, *J. Appl. Polym. Sci.*, **7**, 2121 (1963).
8. W. M. D. Bryant, *J. Polym. Sci.*, **56**, 277 (1962).
9. L. A. Wall and R. E. Florin, *J. Appl. Polym. Sci.*, **2**, 251 (1959).
10. Dr. Chan Chung, Rensselaer Polytechnic Institute, private communication.
11. J. P. Tordella and F. R. Eirich, Eds., *Rheology; Theory and Applications*, Vol. 5, Academic, New York, 1969, Chap. 2.
12. F. W. Billmeyer, *Textbook of Polymer Chemistry*, 2nd ed., Interscience, New York, 1971.
13. J. P. Tordella, *J. Appl. Polym. Sci.*, **7**, 215 (1963).
14. J. P. Tordella, *J. Appl. Phys.*, **27**, 454 (1956).
15. J. H. Golden, *J. Polym. Sci.*, **XLV** (146), 534 (1960).

Received February 8, 1982

Accepted April 1, 1982