

## Maximum Relaxation Times in Polytetrafluoroethylene

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### INTRODUCTION

Much work has been done on the determination of the structure and properties of polytetrafluoroethylene, one of the most interesting of polymers. However, since the polymer is insoluble in all known solvents, the determination of molecular weight by the usual methods is not possible.

Several experimental samples of polytetrafluoroethylene were previously prepared with radioactive sulfur in an iron-bisulfite initiating system.<sup>1-3</sup> The molecular weights of these samples were determined by a counting technique, appropriate but not completely verifiable assumptions being made concerning the end groups of the polymer molecules.

Since radioactive counting could be used only with specially prepared samples, a practical method of determining the molecular weight of polytetrafluoroethylene was devised in which were used the specially prepared samples with radioactive end groups for purposes of calibration. These samples were maintained at 380°C. for 1 hr., cooled at the rate of 1°C./min. to 280°C., and then brought to room temperature where their specific gravity was determined at 25°C. (ASTM D 1457-56T). The following relation was found to hold, although a considerable scatter in the experimental points was obtained:<sup>3</sup>

$$d = -0.0579 \log M_n + 2.6113 \quad (1)$$

where  $d$  is the standard specific gravity and  $M_n$  is the number-average molecular weight determined from the count of the radioactive end groups.

The rationale of eq. (1) is that for a fixed annealing procedure one should expect an inverse relationship between the degree of crystallinity (and hence density) and the molecular weight. It was assumed that eq. (1) would hold approximately for all polytetrafluoroethylene samples, so that specific gravity measurements presumably would provide a practical method of determining the molecular weight of unknown samples.

Experimental limitations of this procedure are (a) that the results depend on a very accurate control of the annealing procedure and (b) that voids in samples give lower values of specific gravity and erroneously large values of molecular weight.

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At this point we should like to introduce a minor proposal. The 10-sec. Gehman modulus (ASTM D 1053-58T), measured at 0°C. after the samples have gone through the ASTM annealing procedure should also give the degree of crystallinity and correlate with the molecular weight. Moreover, this measurement is perhaps somewhat less sensitive to the existence of voids. Values of the 10-sec. Gehman modulus of our samples are incorporated in Table I, together with other measurements to be discussed below.

TABLE I

Poly- mer	Stand- ard <sup>a</sup> spec. gr., g./cm. <sup>3</sup>	$\bar{M}_n^b$	$3G(0),^\circ$ dynes/cm. <sup>2</sup>	$\tau_m$ at 380°C., sec.
B-6046-2	2.175	$3.43 \times 10^7$	$1.31 \times 10^{10}$	55,000
Teflon 1	2.177	$3.17 \times 10^7$	$1.54 \times 10^{10}$	54,000
Teflon 7	2.194	$1.61 \times 10^7$	$1.23 \times 10^{10}$	40,000
Teflon 5	2.200	$1.28 \times 10^7$	$1.81 \times 10^{10}$	38,800
Teflon 6	2.209	$8.88 \times 10^6$	$2.07 \times 10^{10}$	21,000
B-6046-4	2.218	$5.46 \times 10^6$	$3.06 \times 10^{10}$	13,000
T-80	2.223	$5.09 \times 10^6$	$1.85 \times 10^{10}$	5,800
T-16	2.254	$1.48 \times 10^6$	$2.95 \times 10^{10}$	4,000
M-6	2.279	$5.49 \times 10^6$	$3.14 \times 10^{10}$	2,650

<sup>a</sup> Determination after the standard annealing procedure (ASTM D1457-56T).

<sup>b</sup> Molecular weight from the relation between the standard specific gravity and the molecular weight calculated from the concentration of end groups labeled with radioactive sulfur. The calculation is based on the equation  $y = -0.0579x + 2.6113$ , where  $y = \log \bar{M}_n$  and  $x = \log \bar{M}_n$ .

<sup>c</sup> Gehman modulus of annealed samples at 0°C.

## MAXIMUM RELAXATION TIME ABOVE CRYSTALLINE MELTING POINT

In order to overcome the objections to density measurements as practical for determining the molecular weight of polytetrafluoroethylene, we studied the viscoelastic properties of this polymer by the stress relaxation method. These studies were carried out at 380°C., well above the crystalline melting point. They showed the existence of a well-defined maximum relaxation time, since curves of  $\log E_r(t)$  vs.  $t$  showed a very definite linearity for sufficiently long times. The magnitude of the maximum relaxation time has previously been correlated with molecular weight for polystyrene, polyisobutylene, and polyvinylacetate, yielding the following relations:<sup>4,5</sup>

$$\log \tau_m = \log A - [17.44(T - T_g)/(51.6 + T - T_g)] + 3.4 \log n_w \quad (2)$$

where  $\tau_m$  is the maximum relaxation time,  $T$  the temperature of measurement,  $T_g$  the glass transition temperature of the polymer,  $n_w$  the weight-average number of chain links, and  $\log A$  a constant for each polymer. Our studies of maximum relaxation times in polytetrafluoroethylene were designed to discover whether an equation such as eq. (2) was valid for this polymer, at least as far as the dependence on molecular weight was concerned.

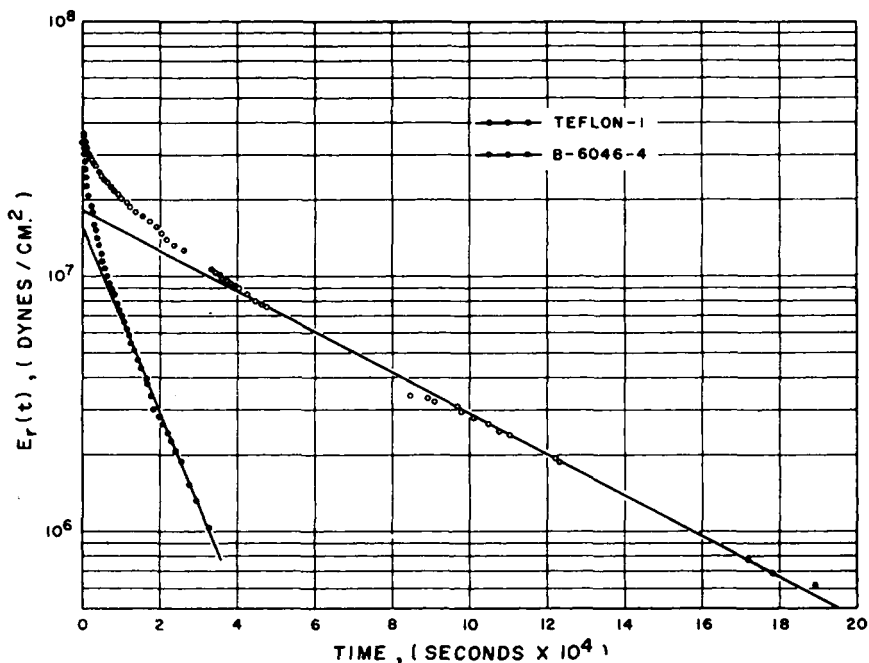


Fig. 1.  $\log E_r(t)$  vs.  $t$  for Teflon and Teflon B-6046-4.

As the curves of  $\log E_r(t)$  vs.  $t$  showed linearity for long periods of time (the time of experiment was two to three times as long as the maximum relaxation time) we felt encouraged in the view that the samples were stable and no appreciable degradation or crosslinking had occurred during our experiments at 380°C. To verify this assumption some of the samples were cooled after the stress relaxation experiments were completed, and then another experiment was run on the very same samples. The same maximum relaxation times were obtained within experimental error, which certainly proves that no degradation had occurred. Earlier experiments by Thomas et al.<sup>6</sup> have also shown that only after samples have been kept for appreciable times at temperatures higher than 390°C. are changes in molecular weight of the polymers noticed.

The linear portions of the plots  $\log E_r(t)$  vs.  $t$  are given by

$$\log E_r(t) = \log E_m - t/2.303\tau_m \quad (3)$$

and the values of  $E_m$  and  $\tau_m$  obtained from stress relaxation runs, are listed for the samples in Table I. Two of the plots of  $\log E_r(t)$  vs.  $t$  at  $380^\circ\text{C}$ . are shown in Figure 1. All of the results of our experiments of the

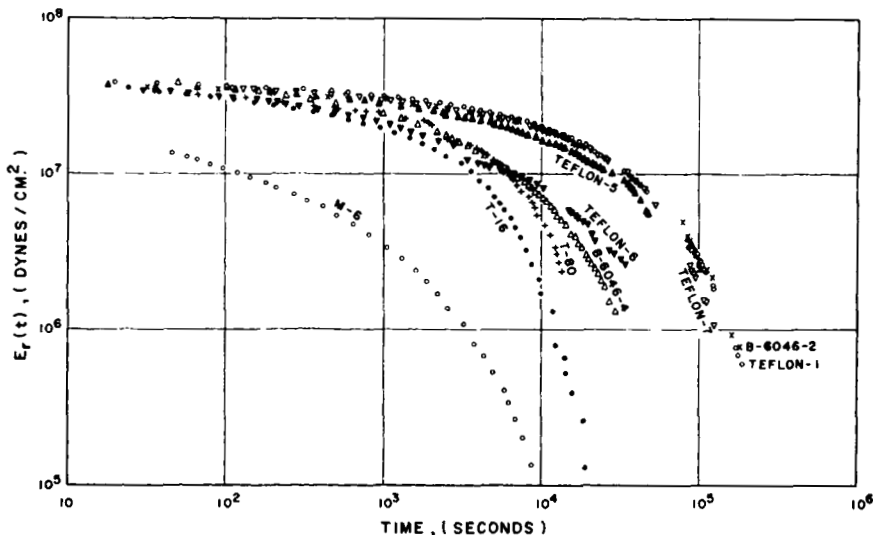


Fig. 2.  $\log E_r(t)$  vs.  $\log t$  for polytetrafluoroethylene samples.

relaxation tensile modulus of different Teflon samples at  $380^\circ\text{C}$ . are given in the log-log plot of Figure 2.

### Materials

The polymers used in our work and listed in Table I are:

1. Teflon 1, 5, 6, 7; commercial samples manufactured by E. I. du Pont de Nemours & Co., Inc.
2. Samples B-6046-2 and B-6046-4, kindly supplied to us by the Research and Development Division of Du Pont.
3. Samples M-6, T-16, T-80; experimental samples.

### Discussion of Results

According to the results listed in Table I, there is a clear correlation between the maximum relaxation time at  $380^\circ\text{C}$ . and the "molecular weight" of the polymer based on the measurements of the standard specific gravity. This correlation is shown in Figure 3. The slope of the straight line in the  $\log \tau_m$  vs.  $\log \bar{M}_n$  plot is equal to 0.78 as against the value of 3.4 in eq. 2. The possible explanations for this are: either polytetrafluoroethylene has flow properties different from those of polystyrene, polyisobutylene, and polyvinylacetate, or the method of determination of

the molecular weight of the polymer, based on measurement of the standard specific gravity, gives only very approximate values.

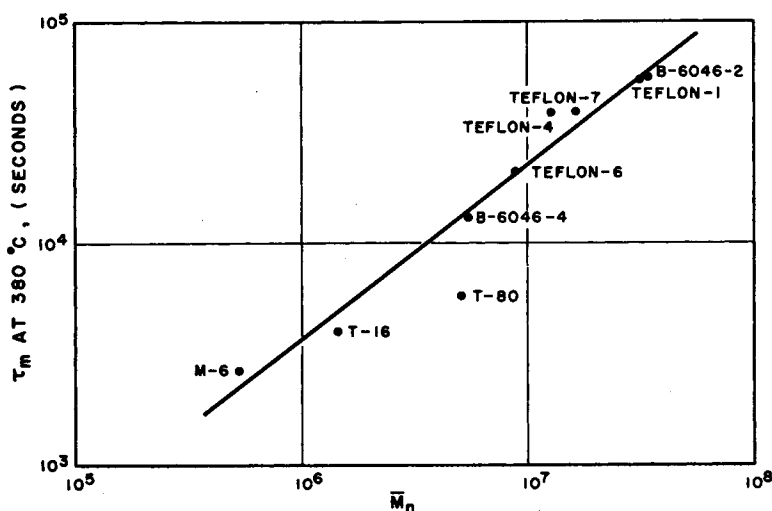


Fig. 3. Log  $\tau_m$  at 380°C. vs. log  $\bar{M}_n$  from standard specific gravity measurements.

### SUMMARY AND CONCLUSIONS

We propose that the measurement of the maximum relaxation time of polytetrafluoroethylene at 380°C. may be used as a nonabsolute method of determining the molecular weight of the polymer. The suggested method is not influenced by the degree of crystallinity, as the measurements are made above the melting point, and it eliminates the necessity of a delicate process of annealing. The temperature of the determination is not high enough to introduce considerable degradation of the polymer, but even in the case of such a reaction's taking place its occurrence would be easily detected by a rerun of the same sample. The sensitivity of this method seems to be quite good; for the range of the tested polymers the standard specific gravity changes from 2.175 to 2.279 gr./cm.<sup>3</sup>, but the maximum relaxation time varies from 2650 to 55,000 sec.

The very large maximum relaxation times in commercial samples of this polymer indicate that these samples are of very high molecular weight, as indicated also by the density measurements. Perhaps these high molecular weights are required to obtain nonbrittle polymers.

It is possible that lower molecular weight samples would be nonbrittle if they were less highly crystalline.

We suggest that a moldable, nonbrittle polymer could be obtained by copolymerizing Teflon monomer with 2-5% of perfluoropropylene and in the presence of a chain transfer agent to control the molecular weight.

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### Synopsis

Molecular weights of polytetrafluoroethylene are presently measured by a density method. We have found that polytetrafluoroethylene exhibits a sharply defined maximum relaxation time,  $\tau_m$ , above its melting point. There is a clear correlation between  $\tau_m$  at 380°C. and the "molecular weight"  $M_n$  of the polymer based on the measurement of density. However,  $\log \tau_m$  vs.  $\log M_n$  gives a slope of 0.78 as against a value of 3.4 obtained for other polymers. Either polytetrafluoroethylene has flow behavior very different from other polymers or the molecular weight of the polymer based on the measurement of density is only approximate.

### Résumé

Les poids moléculaires du polytétrafluoroéthylène sont actuellement déterminés par une méthode densitométrique. Nous avons trouvé que le polytétrafluoroéthylène présente un temps de relaxation maximum parfaitement défini au delà le son point de fusion. Il existe une corrélation nette entre le temps de relaxation maximum  $\tau_m$  à 380°C et le "poids moléculaire"  $M_n$  du polymère basé sur une mesure de densité. Lorsqu'on porte  $\log \tau_m$  en fonction de  $\log M_n$  on obtient cependant une tangente de 0.78 assez différente de la valeur de 3.4 obtenue pour d'autres polymères. Ceci résulte pour le polytétrafluoroéthylène soit d'un comportement à l'écoulement très différent de celui des autres polymères soit d'une mesure densitométrique approximative du poids moléculaire de ce polymère.

### Zusammenfassung

Das Molekulargewicht von Polytetrafluoräthylen wird gegenwärtig nach einer Dichtemethode gemessen. Wir haben gefunden, dass Polytetrafluoroäthylen oberhalb des Schmelzpunktes eine scharf definierte maximale Relaxationszeit besitzt. Es besteht eine klare Beziehung zwischen der maximalen Relaxationszeit  $\tau_m$  bei 380°C und  $M_n$ , dem "Molekulargewicht" des Polymeren aus der Dichtemessung.  $\log \tau_m$  gegen  $\log M_n$  ergibt jedoch eine Neigung von 0,78 verglichen mit einem Wert von 3,4 für andere Polymere. Entweder besitzt Polytetrafluoroäthylen ein von anderen Polymeren sehr verschiedenes Fließverhalten oder das Molekulargewicht des Polymeren aus der Dichtemessung ist nur ein Näherungswert.

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