# Evaluation of Number-Average Molecular Weight of Poly(tetrafluoroethylene) Irradiated with γ Rays

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## Synopsis

The number-average molecular weight of poly(tetrafluoroethylene) (PTFE) irradiated from a ^{60}Co source in air at room temperature has been estimated from the experimental results of tensile creep measurements and electron microscopy. The viscoelastic method which makes use of the maximum relaxation time was used for samples with low radiation doses. The mean chain length of highly irradiated samples, which can form fully extended chain crystals upon crystallization from the melt, was obtained from the bandwidth distribution on micrographs of the fracture surfaces. The dependence of the average molecular weight on the radiation dose is derived on the basis of a statistical treatment in which effects of cages in the process of chain scission and of molecules evolved out of the specimen, together with random decomposition of polymer backbone chains, are considered. Good agreement between the experimental and calculated results is attained over a wide range of radiation doses.

## INTRODUCTION

Poly(tetrafluoroethylene) (PTFE) polymer is insoluble in the usual solvents. The determination of its molecular weight necessarily comes from specialized, indirect molecular weight methods. A counting technique[1] for estimating the molecular weight can be used only with the specially prepared PTFE samples containing radioactive end groups. The density method,[2,3] which is more practical, involves a standard annealing procedure before the measurement. Tobolsky, Katz, and Eisenberg[4] have indicated that the number-average molecular weight of PTFE can be determined from the "maximum relaxation time," which is not affected by the degree of crystallinity at room temperature, and the method eliminates the necessity of a delicate process of heat treatment. Suwa, Takehisa, and Machi[5] proposed a relationship for estimating the number-average molecular weight of PTFE from the heat of crystallization. The number-average molecular weight of commercial PTFE is usually of the order of $10^6$–$10^7$.

When PTFE samples are exposed to γ irradiation, scission of polymer backbone chains occurs; this radiation effect results in the decrease in average molecular weight.[6–9] Explicit experimental data of average molecular weight for irradiated PTFE were given by Bro[10] and Ferse[11] and their co-workers. In particular, the number-average molecular weight for PTFE samples which received doses below $1 \times 10^6$ R was given according to Sperati's and Osten's relationships.[2,11]

Several theoretical treatments of the reduction in average molecular weight have been carried out in linear polymers of the degradation type.[7,8,12–17] In the simple case where polymer chains are broken in a random manner at a rate di-

rectly proportional to the radiation dose, the statistical theory indicated that a linear relationship exists between the reciprocal of the number-average molecular weight and the radiation dose.[7]  For instance, a detailed investigation of the radiation degradation of polyisobutylene gave such a linear curve.[7,8,12]

The purpose of this article is to deal with a quantitative evaluation of number-average molecular weight for irradiated PTFE samples.  The results reported here are analyzed with the aid of a theory developed by Sakurada and Okamura[15] for the decomposition of linear polymers.  A cage effect in the process of chain scission and evolution of small molecules, together with random decomposition of linear polymers, are considered.  Experimental data on the average molecular weight are obtained from the viscoelastic method and from electron microscopy. Furthermore, the results of small-angle x-ray scattering measurements are discussed for PTFE samples which received doses above $10^9$ R.

## EXPERIMENTAL

### Materials

The original PTFE and most of the irradiated samples are the same as those used previously in density measurements.[18]  Irradiation was carried out with a $^{60}$Co source in air at room temperature.  The exposure dose rate is $1.05 \times 10^5$ R/hr.  The radiation dose is in the range $(3.2 \times 10^3)$–$(2 \times 10^8)$ R.  The exposure radiation dose can be changed into the corresponding absorbed dose by the conversion factor for $\gamma$ irradiation, i.e., 0.84 rad (in PTFE)/R (air).[19,20]  Tensile creep measurements were made for samples with low radiation doses up to $1 \times 10^5$ R, and electron microscopy was carried out for highly irradiated samples with doses of $1 \times 10^8$ and $2 \times 10^8$ R.

### Tensile Creep Measurements

Tensile creep behavior has been studied in the molten state of low-irradiated PTFE.[21]  The experimental results here were used only for determining an average molecular weight of the samples.

Measurements in tensile creep were made with a conventional apparatus of a balance type.  The displacement of the sample was measured by a linear variable differential transformer.  Specimen temperature was controlled within ±0.2°C at temperatures below 380°C.  Each sample was held at a measuring temperature for at least 3 hr to ensure complete melting.

According to the time–temperature superposition principle,[22] the master curve $D_p(t)$ was obtained by shifting the curves for the tensile creep compliance measured at different temperatures below 375°C, as shown in Figure 1.  The shift factor $a_T$ used in this reduction followed the WLF equation[22,23]:

$$\log a_T = \log A - 17.44(T - T')/(51.6 + T - T')$$

with $T' = 125°C$, where $A$ is a constant ($\log A = 14.2$).  The subscript $p$ denotes that the compliance has been multiplied by $T\rho/T_0\rho_0$, where $\rho$ is the density at a temperature of measurement and $\rho_0$ is the density at a reference temperature $T_0$.  The reference temperature was chosen as 350°C for all the samples.  Values of $\rho$ were calculated from a thermal expansion coefficient of $6.2 \times 10^{-4}$ °C$^{-1}$ and $\rho_0$ of 1.515 g/cm$^3$.
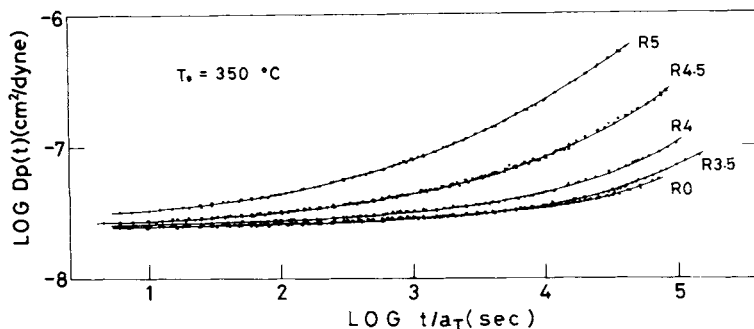
Fig. 1. Master curves for tensile creep compliances of $\gamma$-irradiated PTFE samples: sample R0, unirradiated; R3.5, $3.2 \times 10^3$ R; R4, $1 \times 10^4$ R; R4.5, $3.2 \times 10^4$ R; R5, $1 \times 10^5$ R. Reduced temperature is 350°C for all samples.

In order to determine the number-average molecular weight from the maximum relaxation time,[24] the relaxation modulus $E(t)$ was first derived from the master curve $D_p(t)$ using the approximate relation[22]

$$E(t) = \frac{\sin m\pi}{m\pi \, D_p(t)}$$

where $m = d[\log D_p(t)]/d[\log t]$ and $m < 1$. The values of $m$ used are smaller than 0.7. The maximum relaxation time was estimated from the obtained modulus $E(t)$ by use of Tobolsky's procedure X.[24] Table I shows the number-average molecular weight $\langle M_n \rangle$ evaluated according to the relation of $\langle M_n \rangle$ against Tobolsky's "maximum relaxation time" for PTFE samples.[4] Here $\langle M_n \rangle$ of the unirradiated PTFE is $2.2 \times 10^7$ and appears to be comparable to the molecular weight values in the literature.[2-5] It should be noted that values of the average molecular weight determined for PTFE have been obtained on the basis of some appropriate but not completely verifiable assumptions.[2-5]

TABLE I
Number-Average Molecular Weight of Irradiated PTFE Samples

| Sample | Radiation dose $r$, R | Number-Average molecular weight[a] | Mean chain length,[b] nm |
|---|---|---|---|
| R0 | unirradiated | $2.2 \times 10^7$ | — |
| R3.5 | $3.2 \times 10^3$ | $2.5 \times 10^7$ | — |
| R4 | $1 \times 10^4$ | $2.5 \times 10^7$ | — |
| R4.5 | $3.2 \times 10^4$ | $1.6 \times 10^7$ | — |
| R5 | $1 \times 10^5$ | $5.7 \times 10^6$ | — |
| AR8 | $1 \times 10^8$ | $\sim 3 \times 10^4$ | $\sim 70$ |
| 2AR8 | $2 \times 10^8$ | $\sim 2.5 \times 10^4$ | $\sim 65$ |
| 1.4AR9 | $1.4 \times 10^9$ | $9.6 \times 10^3$ | 25 |
| 1.7AR9 | $1.7 \times 10^9$ | $7.9 \times 10^3$ | 20.5 |
| 2.9AR9 | $2.9 \times 10^9$ | $5.4 \times 10^3$ | 14 |

[a] The last five samples: from the mean chain length in the next column.
[b] Samples AR8 and 2AR8 from the mean bandwidth; samples 1.4AR9, 1.7AR9, and 2.9AR9 from the results of SAXS.[39]

## Electron Microscopy

The morphology of highly irradiated PTFE was observed with two-stage replicas of fracture surfaces. The PTFE samples which received doses of $1 \times 10^8$ and $2 \times 10^8$ R were treated at a cooling rate of about 3°C/hr from the melt-down to about 200°C to obtain sufficient crystallization (samples AR8 and 2AR8). Fractures were made at room temperature owing to the brittleness of the samples. Replicas of fracture surfaces were prepared by replicating first with a cellulose acetate film and afterward by forming a platinum–carbon membrane. The electron microscope was a JEOL model JEM-7 (Japan Electron-Optics Laboratory Co., Ltd., Tokyo, Japan).

The distribution of bandwidths was obtained from micrographs of fracture surfaces. The procedures used are principally the same as a method by Bassett and co-workers.[25,26] The technique consists of drawing arbitrary lines on the micrograph and for each line measuring the bandwidth parallel to striation (c axis) at the region of intersection for every layer crossing that line. The data of bandwidths are presented in a frequency histogram. The estimate gives a number-average distribution because each band is counted once. The absolute value of length was checked by calibration of the electron microscope against a standard grating. Figures 2(a) and 2(b) show typical micrographs of fracture surfaces for samples AR8 and 2AR8, respectively. The mean bandwidths of these samples are given in Table I.



(a)                                                    (b)
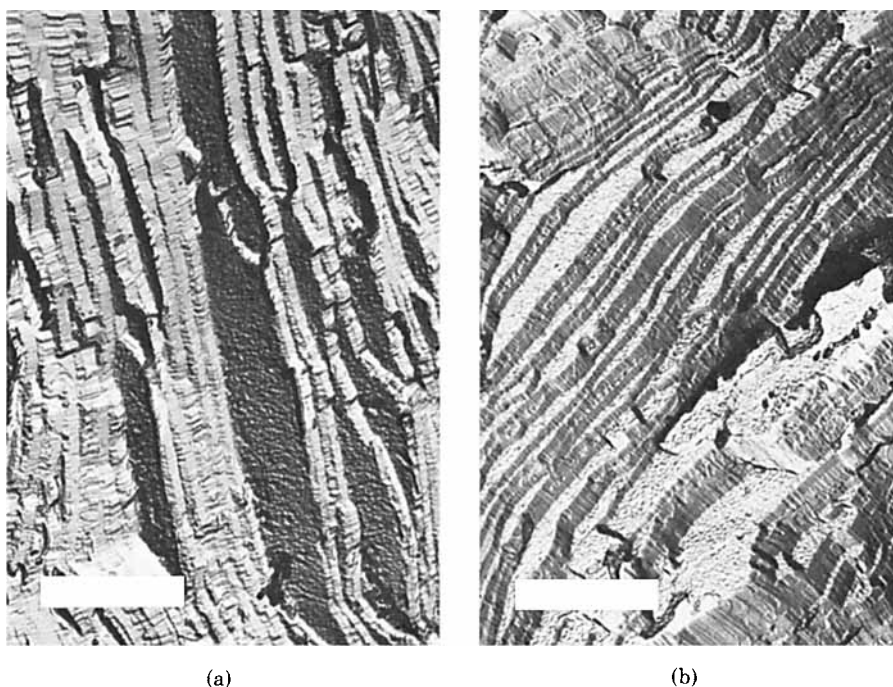
Fig. 2. Typical electron micrographs of fracture surfaces for PTFE samples irradiated with doses of $1 \times 10^8$ R (a) and $2 \times 10^8$ R (b). Bar denotes 1 $\mu$m.

## RESULTS AND DISCUSSION

### Theoretical Treatment

A specimen is considered to consist of $n$ chains, each of which has $N + 1$ monomer units on the average. Therefore, the total number of bonds in the system is $nN$. If the number of scissions, $x$, occurring per chain molecule is not extraordinarily large and $n$ is large enough, the scission density $P$ is approximately equal to $nx/nN = x/N$.[15] Here, $P$ is treated as the probability of occurrence of a chain scission, while the probability that a given bond does not break is given by $1 - P$. Furthermore, it is assumed that scission of any bond in a chain is equally probable and takes place in a random manner. Thus, the number of chain fractions with $m$ units is given by $A_m = n(N - m)P^2(1 - P)^{m-1}$ in the case of breaking a chain molecule at any two bonds, and by $A'_m = 2nP(1 - P)^{m-1}$ when the effect of chain ends is considered.[15] Further, the number of nondegraded chains is given by $A_N = n(1 - P)^N$.

Random chain scission of backbone chains caused by $\gamma$ irradiation results in a molecular weight distribution to be a wide fraction, irrespective of the initial distribution of the sample.[8,27] Short-chain molecules also increase with increasing radiation dose. It may be expected that shorter-chain molecules below a degree of polymerization in the chain fraction should be evolved during irradiation and by subsequent heat treatments. It is possible also that a high temperature in thermal treatments accelerates evolution of small molecules, partly by accompanying pyrolysis.[28] If molecules with monomer units less than $l_0 + 1$ in the molecular weight distribution are evolved, the number-averaged molecule after such evolution has $\langle l_n \rangle$ units, where

$$\langle l_n \rangle = \frac{\sum_{m=l_0-1}^{N-2} mA_m + \sum_{m=l_0}^{N-1} mA'_m + (N + 1)A_N}{\sum_{m=l_0-1}^{N-2} A_m + \sum_{m=l_0}^{N-1} A'_m + A_N} \tag{1}$$

Summation with respect to $m$ leads to (assuming that $P \ll 1$)

$$\langle l_n \rangle = \frac{(N + 1) + Pl_0(N - l_0)}{1 + P(N - l_0)} \tag{2}$$

The sample of PTFE may be regarded as a two-phase system consisting of crystalline and amorphous regions in this study. A difference in susceptibility to radiation damage is expected between the two phases. This may be explained in terms of a cage effect in the chain scission process[7,18]; the increased strain and loose packing of polymer chains involved in the amorphous phase facilitate escape of chain ends from a cage by diffusion. Therefore, chain scissions caused by irradiation are more dominant in the amorphous phase than in the crystalline phase.[18]

The scission densities for the crystalline and amorphous parts are represented as $P_c$ and $P_a$, respectively. If $n_c$ chains belong to the crystalline part and $n_a$ to the amorphous part, the effective scission density $P_e$ is expressed in the form

$$P_e = P_a + (P_c - P_a) n_c/n$$

$$= (1 - w^c)P_a + w^c P_c \tag{3}$$

since $n = n_c + n_a$ and the degree of crystallinity $w^c$ is assumed to be $n_c/n$; that is, $w^c$ is defined as the number of monomer units in the crystalline part per chain unit. If $P_c$ is negligible compared to $P_a$, by considering the cage effect $P_e$ is given by

$$P_e \simeq (1 - w^c)P_a$$

$$= \phi P_a \qquad (4)$$

where $\phi$ is the amorphous fraction, equivalent to $n_a/n$.

The relation between $P_a$ and radiation dose $r$, for random degradation owing to high-energy $\gamma$ irradiation, is given by $P_a = qr$ or $r/(N + 1)r_0$, to a satisfactory approximation, where $q$ is the proportion of monomer units broken per unit radiation dose and $r_0$ is the radiation dose at which one break takes place per chain molecule.[18] The dependence of amorphous fraction on $r$ for irradiated PTFE has been expressed in the relation

$$\phi = \phi_0 \left( \frac{r}{r_0'} + 1 \right)^{-0.12}$$

where $\phi_0$ is the initial amorphous fraction of the sample and $r_0'$ is the characteristic radiation dose, which is nearly equal to $r_0$.[18] The ratio $r_0'/r_0$ depends upon the distribution of molecular weights of the initial polymer.[18] If the initial polymer is a narrow fraction having a uniform molecular weight distribution, then $r_0'/r_0 \sim 2$, whereas if this polymer has a random distribution, then $r_0'/r_0 \sim 1$. It seems likely that $1 \lesssim r_0'/r_0 \lesssim 2$ for the real PTFE samples. These treatments have been discussed in detail elsewhere.[18]

Therefore, using the effective scission density $P_e$ and assuming the initial sample to be a narrow fraction,[29] eq. (2) can be rewritten as

$$\langle l_n \rangle = \frac{(N + 1) + P_e l_0 (N - l_0)}{1 + P_e (N - l_0)} \qquad (5)$$

where

$$P_e = \frac{2\phi_0}{N + 1} \frac{r}{r_0'} \left( \frac{r}{r_0'} + 1 \right)^{-0.12}$$

### Comparison with Experiment

The number-average molecular weight of irradiated PTFE is estimated from eq. (5) using $N + 1 = 4.4 \times 10^5$, $\phi_0 = 0.416$, and $r_0' = 2.7 \times 10^4$ R. The last two values have previously been evaluated from the results of the density measurements for the same samples.[18] Furthermore, $l_0 + 1 = 10$ may be regarded as a measure of small molecules evolved from the sample [when $k = 10$ for $F(CF_2)_k F$, the boiling point is 144°C].[30] Figure 3 shows the curve calculated by substituting the above values into eq. (5), and it appears that the effect of small molecules evolved becomes important in the dose region above $10^8$ R.

The experimental results obtained by the viscoelastic method show that the average molecular weight is almost the same up to doses of $10^4$ R and subsequently begins to decrease as the radiation dose is increased. At doses less than $10^4$ R, the slight increase in the molecular weight may be due to such effects as radiation-induced crosslinking,[31] but these radiation effects are not considered
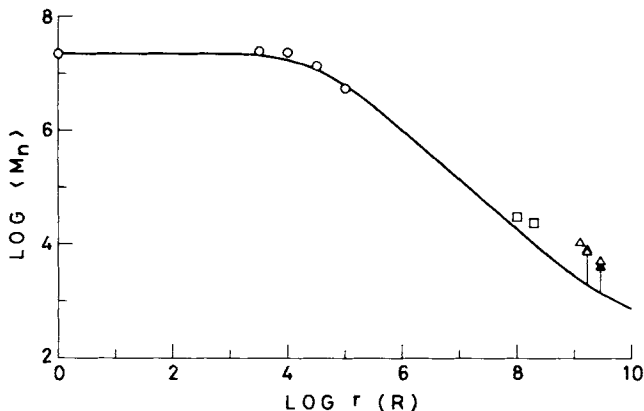
Fig. 3. Number-average molecular weight of PTFE samples as function of radiation dose: solid curve calculated by substituting $N + 1 = 4.4 \times 10^5$, $r_0' = 2.7 \times 10^4$ R, $\phi_0 = 0.416$, and $l_0 + 1 = 10$ into eq. (5) and experimental data. (O) Viscoelastic method; ($\square$) electron microscopy; ($\triangle$) SAXS; ($\blacktriangle$) $\langle M_n \rangle$ modified by the effect of compounds evolved. The value for unirradiated polymer is indicated on the ordinate.

further in this investigation. A remarkable decrease in molecular weight takes place at a dose of $10^4$ R, which also corresponds to an inflection for the melt viscosity,[6,21] which is sensitive to molecular weight; this indicates the occurrence of a large number of chain scissions caused by irradiation. The experimental data of the PTFE samples that received doses below $10^5$ R could be fitted to the calculated curve, as shown in Figure 3.

The average molecular weight of samples AR8 and 2AR8 was obtained from the distribution of bandwidths on micrographs of fracture surfaces. It is known that melt-grown crystals of the unirradiated and low-irradiated PTFE with large chains show band structures[32] whose width is not usually in agreement with chain length.[33,34] It has been suggested,[35] however, that PTFE samples of low molecular weight are able to crystallize into fully extended chain crystals[36] through certain processes of crystal growth. As the decrease in chain length proceeds, greater mobility in the melt allows to segregate on crystallization and to form the bands with different thickness, likely comparable to chain lengths.[36] Samples AR8 and 2AR8, which were crystallized from the melt at a cooling rate of 3°C/hr, showed several kinds of experimental evidence for the formation of fully extended chain crystal. Micrographs for these samples exposed large amounts of sufficiently developed (001) surfaces, as shown in Figure 2. No significant variation in mean bandwidth with time and temperature have so far been observed in highly irradiated PTFE,[37] unlike the unirradiated and low-irradiated samples with large molecular weights.[34,38] Furthermore, the chain stiffness of a PTFE polymer and the reduction of chain length may perhaps influence the growth of crystals consisting of extended chains.

The mean chain length obtained from the population of bandwidths is slightly larger than the calculated length, as Figure 3 shows in molecular weight. It seems likely that the mean bandwidth depends upon small molecules evolved out of the specimen during thermal treatments, because materials evolved have been seen in the sample vessel after heat treatments for these samples. This effect is later discussed for more highly irradiated PTFE. It should be noted that errors in reading on bandwidth and correction for the presence of smaller crystals whose

size is below the level of resolution of two-stage replication have not been taken into account in the procedure of estimating the mean bandwidth.

The average molecular weight of PTFE samples more highly irradiated, with doses more than $10^9$ R, was determined from the results of small-angle x-ray scattering (SAXS) measurements.[39] These samples include many short-chain oligomers by radiation-induced scission. Microscopic morphology reveals formation of band structures of multilayers on the fracture surfaces of these samples, as well as of samples AR8 and 2AR8, when crystallized by a slow cooling from the melt. It is difficult to measure from micrographs of the fracture surfaces different widths of long bands that are stacked because of the very small thickness of these bands. The long period of these samples by SAXS measurements, therefore, was undertaken and the obtained results may correspond to the mean width of the bands which were stacked in multilayers. It should be pointed out also that massive radiation doses cause changes in the polymer that appear to involve formation of branched structures,[20,40] together with production of short-chain oligomers by chain scission.[41] Branching brings about the increase in chain flexibility and in intermolecular distance in crystalline regions where branches such as $CF_3$ are included as defects.[42,43]

In view of similar evidence described above for samples AR8 and 2AR8, however, it may be expected that short-chain molecules segregate on crystallization and form long bands whose thickness is comparable to chain lengths shortened by radiation-induced chain scission. It is worth noting that similar behavior has been obtained in other polymers for a variety of crystallization conditions.[36]

The values of average molecular weight obtained from the long period of the irradiated samples are considerably higher than those calculated from eq. (5), as shown in Figure 3. This difference in magnitude may be due to evolution of shorter chain molecules generated on $\gamma$ irradiation by thermal treatment at higher temperatures. It has been reported that when $\gamma$-irradiated samples in the presence of oxygen, the principal volatile products are carbonyl fluoride, constituting a large percentage of the gas, $SiF_4$ (in glass container), and $CO_2$ in small amounts.[9,44] The effect of the volatile products on the average molecular weight is considered to be poorer than that of chain scissions owing to irradiation. In a postirradiation treatment, short-chain molecules produced by irradiation at room temperature are thermally degraded and further evolved from the sample which was kept at elevated temperatures.[9,28]

For the measurement of SAXS, the sample irradiated with doses of $1.7 \times 10^9$ R (sample 1.7AR9) was kept at 310°C for about 2 hr before a process of crystallization began. The melting temperature of this sample drops considerably to about 250°C.[45] The depression of the melting point of this sample may depend on the inclusion of defects in the crystals and the decrease in crystal sizes, i.e., bandwidths corresponding to chain lengths shortened by scission.[40,42] The maximum temperature of this sample experienced during heat treatment appears to be sufficiently high to cause thermal degradation and to boil off shorter chains.[9,28] In addition, thermogravimetric (TG) analysis was made for sample 1.7AR9; the results indicated that the weight loss was about 85% after being kept for 2 hr in the liquid state at 310°C. The considerable weight loss may arise from the evolution of small molecules produced mainly by radiation damage. When pyrolysis and oxidative decomposition took place during postirradiation thermal
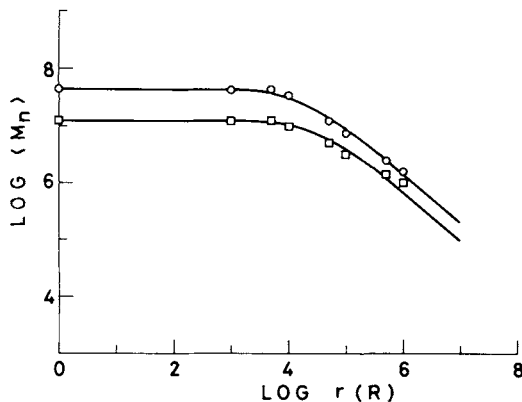
Fig. 4. Numer-average molecular weight of PTFE samples as function of radiation dose. Solid curves are calculated from eq. (5) for Sperati's data (O), using $N + 1 = 9.4 \times 10^5$, $r_0' = 1.7 \times 10^4$ R, $\phi = 0.455$; and for Osten's data ($\square$), using $N + 1 = 2.6 \times 10^5$, $r_0' = 3.2 \times 10^4$ R, $\phi_0 = 0.455$. In this calculation, $l_0 + 1$ is neglected. The point on the ordinate is for the unirradiated polymer.

treatments, most of the resulting compounds are also evolved out of the sample during the treatment.

An attempt is made to estimate roughly an average chain length or molecular weight by considering the effect of the gases evolved. It is assumed that the most probable distribution of molecular weights, of which $\langle M_n \rangle$ is derived from eq. (5), can reasonably be applied to the PTFE samples which received high radiation doses[8,27] and that species at the lower end of the molecular weight distribution are preferentially evolved from the specimen. Thus, the weight loss of about 85% for the 1.7AR9 sample leads approximately to a mean chain length of 21.5 nm. This value is consistent with that of 20.5 nm obtained from the results of SAXS.[39] A similar estimation of the sample which received doses of $2.9 \times 10^9$ R (sample 2.9AR9) gave about 11 nm in chain length, whereas the chain length estimated from data of SAXS was about 14 nm.

Sperati's and Osten's data[9] on the number-average molecular weight for irradiated PTFE provides further verification of the derived relation in eq. (5). The value of the unknown parameter $r_0'$ is determined by the fitting method. The former data gave a value of $1.7 \times 10^4$ R for $r_0'$ and, by definition, led to a $G$ value (scission) of 4.8 by using $N + 1 = 9.4 \times 10^5$. The latter gave a value of $3.2 \times 10^4$ R for $r_0'$, which corresponds to a $G$ value (scission) of 8.8. The curves calculated here fit their data well, as shown in Figure 4.

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